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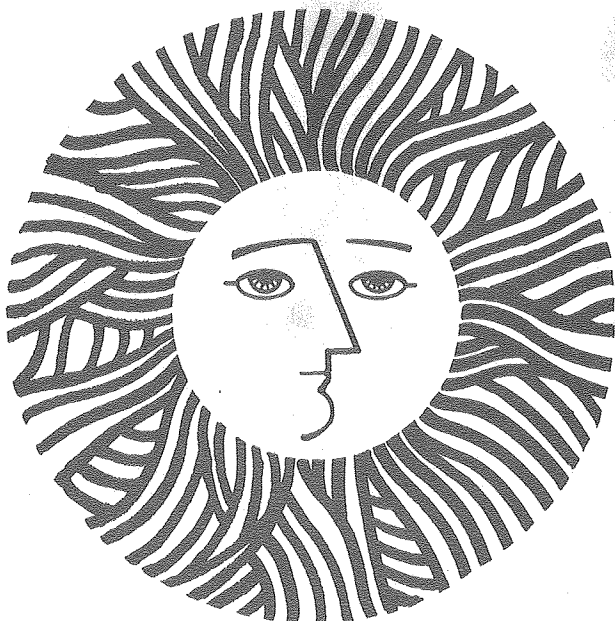
STRIPPING OF PROCESS CONDENSATES FROM SOLID
FUEL CONVERSION

Joel David Hill
(M.S. thesis)

June 1980

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SOLID FUEL CONVERSION

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Joel D. Hill

"Stripping of Process Condensates from
Solid Fuel Conversion"

ABSTRACT

Process condensates from the Solvent Refined Coal (SRC) Test Facility (Fort Lewis, Washington) and from the Omega-9 in situ oil shale retorting test (Rock Springs, Wyoming) were stripped batchwise at approximately 20°C using nitrogen. The gases leaving these solutions were passed through a train of absorbers, taking up ammonia and acid gases (carbon dioxide and hydrogen sulfide) successively. The amount of hydrogen sulfide absorbed was differentiated from carbon dioxide by selective precipitation as CuS using CuCl_2 solution.

The solute concentrations (ammonia, carbon dioxide and hydrogen sulfide) in the solutions being stripped were measured by means of Orion specific-ion electrodes. These solute concentrations were determined at regular intervals throughout the stripping process; the concentration changes of the solutes were typically at most 5% during the interval between vapor pressure measurements. Stripping was continued until the indicated vapor pressures of all three volatile solutes fell below 0.01 mmHg. At this point either the solute was completely removed from the solution or the solute was held in solution by stoichiometric equivalence with one or more non-volatile cations or anions,

and the pH began to change rapidly.

The acid gases (carbon dioxide and hydrogen sulfide) in the SRC condensate water were highly volatile during the initial stripping when the pH was less than 9.2 (initial pH of 8.8). The hydrogen sulfide vapor pressure was much higher than that of carbon dioxide until most of the hydrogen sulfide was removed. The ammonia was not as volatile as the acid gases until enough of the acid gases were removed and the pH began to rise above 9.4. The stripped SRC condensate water contained no measurable carbon dioxide and hydrogen sulfide, but about 0.46 moles/liter of ammonia was held into solution in a non-volatile form, with a final pH of the stripped water of 7.5. Hence gravimetric analyses were made for chloride (Cl^-) and sulfate ($\text{SO}_4^{=}$), and an iodometric titration was used for thiosulfate ($\text{S}_2\text{O}_3^{=}$) analyses.

There was about a 15% loss of sulfide throughout the stripping, which is believed to have been oxidized. Also, after the sulfide concentration dropped below 10^{-5}M , the solution showed signs of further oxidation, turning dark and murky, which indicates oxidation of phenolic compounds. The darkening of the solution was accompanied by a loss in carbon dioxide from the solution, believed to have been consumed in a reaction.

Carbon dioxide came out of the Omega-9 retort water readily at first with initial pH of 8.6, but the volatility of ammonia was suppressed until enough of the carbon dioxide

was removed to raise the pH above 9.2. The pH continuously rose during the stripping to a final value of 10.2 and 99% of the ammonia was removed from the retort water. Approximately 0.06 moles/Liter of carbon dioxide remaining in the stripped water appeared to be paired with non-volatile cations, which were primarily Na^+ .

The results are interpreted in terms of existing models of vapor-liquid equilibria in solutions of volatile weak electrolytes, and in terms of the indicated concentrations of other cations and anions.

Chapter I. Stripping of Process Condensate

A. Introduction

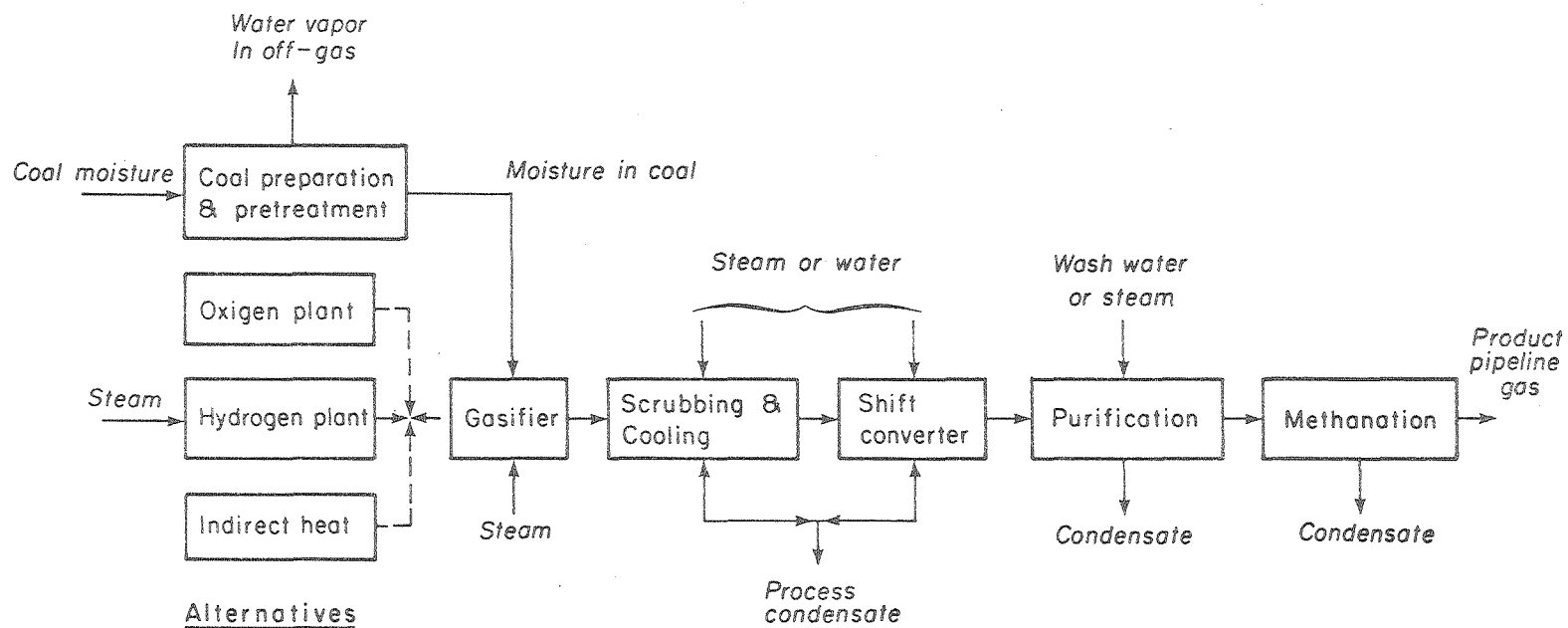
With the domestic supply of readily available petroleum and natural gas declining, the United States has become heavily dependent on imported fuel supplies for its energy needs. This provides a strong incentive for developing alternative fuels, such as coal, oil shale and tar sands. It is desirable to convert these resources into liquid or gaseous fuels for convenient use.

Solid fuels generally have a low hydrogen/carbon ratio, as compared to gaseous and liquid fuels. Upgrading these solid fuels requires hydrogenation, for which the most economical source of hydrogen is water, which must be fed as liquid water or steam to the conversion reactor. Water is also commonly used for quenching the reactor effluent, and for driving the water-gas shift reaction



to completion in a coal gasification process. Water usage and management in solid-fuel conversion processes are discussed by Water Purification Associates (1977), Probststein and Gold (1978), and King, et al (1979).

Usually the most contaminated water in a coal conversion or shale retorting process is foul process condensate which is formed by condensing steam present in hot reactor effluents. Sources of process condensate for a typical coal gasification process are shown in Figure I-1. The condensates



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Figure I-1. Water streams in a plant to produce pipeline gas from coal.
Taken from Water Purification Associates (1977).

from scrubbing and cooling and from shift conversion are more contaminated than those from subsequent points in the process, since these condensates are the first to be removed from the reactor effluent.

B. Flow Rates and Compositions

The foul process condensate flow from solid-fuel conversion varies widely from process to process. For a 3×10^{11} Btu/day Solvent Refined Coal plant a typical flow is approximately 1,000 gal/min (Water Purification Associates, 1977). The physical size of such a stream can be envisioned as water flowing through a 6-inch diameter pipe at 10 ft/sec. The composition of a process condensate from the Pittsburgh and Midway Solvent Refined Coal pilot plant in Dupont, Washington is given in Table I-1.

The composition of retort water (process condensate) from an in situ shale retorting process is given in Table I-2. The analysis in Table I-2 is for the Omega-9 test (Rock Springs, Wyoming, 1976), and is a composite of analyses from many laboratories (Farrier, et al., 1979).

C. Environmental and Recycle Concerns; Processing Steps

One can readily see that these condensate waters cannot be released to rivers, lakes, etc., for environmental reasons. In fact, there is usually a large incentive for somehow recycling condensate waters as cooling tower make-up, as quench water to the process, as boiler feed water, or in some other way.

TABLE I-1

ANALYSIS OF PROCESS CONDENSATE
PITTSBURGH AND MIDWAY SOLVENT
REFINED COAL PILOT PLANT

SHIPMENT SAMPLE NO. 1692
Sample Taken: 12/11/79
Analysis Performed: 1/10/80

Total Ammonia	2.95	M ^a	(Moles/Liter)
Inorganic Carbon	1.25	M ^a	
Hydrogen Sulfide (as HS)	0.91	M ^a	
Phenol	3200	ppm ^b	
Resorcinol	3200	ppm ^b	
Acetate	c		
pH	8.77	^a	
Chemical Oxygen Demand	30,000	ppm ^b	

Notes:

- a. This work.
- b. Don Mohr, personal communication.
- c. Not measured.

TABLE I-2

Omega-9 Retort Water Analysis
 Taken From Farrier, et al. (1979)

Total Ammonia	0.22 M
Inorganic Carbon	0.29 M
C O D	8100 ppm
pH	8.62

Non-volatile Ions

		eg. wt./L
Mg ⁺⁺	0.001 M	.002
K ⁺	0.001 M	.001
Na ⁺	0.188 M	<u>.188</u>
		.191
Cl ⁻	0.023 M	0.023
F ⁻	0.003 M	0.003
SO ₄ ⁼	0.021 M	0.042
S ₂ O ₃ ⁼	0.024 M	0.048
S ₄ O ₆ ⁼	0.001 M	0.002
SCN ⁻	0.002 M	<u>0.002</u>
		0.120

The principal processing treatment operations which have usually been proposed are extraction for removal of phenols and other materials contributing to the COD (Chemical Oxygen Demand), stripping to remove ammonia accompanied by carbon dioxide and hydrogen sulfide, bio-treatment for degradation of organics, and carbon adsorption and/or ozonation as finishing steps. (Oldham and Wetherold (1977); King, et al., 1979)). The stripping operation is the focus of this thesis.

Stripping removes the ammonia, carbon dioxide and hydrogen sulfide from the condensate stream. Removal of ammonia and hydrogen sulfide is necessary for the water to be recycled as boiler feed or cooling-tower makeup. Ammonia would also interfere with subsequent biological treatment. Removing the acidic and basic gases reduces the buffering effect caused by those solutes, so that the pH can be more easily adjusted, if desired, for subsequent processing. With the ammonia and carbon dioxide present, the use of chemicals for pH adjustment would be prohibitively expensive and would lead to high salt content in the treated water.

Stripping of ammonia and the acid gases is complicated by the ionization of these substances in solution. The acid-base reaction between the two leads to a pH of about 9, at which point the extent of ionization is high for ammonia, carbon dioxide and hydrogen sulfide. At 25°C and a pH of 9.0, 65% of the total NH_3 is ionized to NH_4^+ and 99% of

each of the CO_2 and H_2S are ionized to HCO_3^- and $\text{CO}_3^{=}$ and HS^- respectively. The ionization considerably suppresses the volatilities of the gases, since the Henry's Law relationship applies to only the un-ionized form.

Calculations of expected steam requirements for stripping of ammonia and the other gases from process condensates lead to boil-up requirements of from 5 to 20% of the water, depending upon the concentration and composition of the water (Verhoff and Choi (1979); Oldham and Wetherold (1977)). If steam costs \$3.00 per thousand lbs., a boil-up ratio of 15% would correspond to a water treatment processing cost of \$3.75/1,000 gallons for stripping steam alone! If separation of ammonia from the acid gases is desired, a more complex stripping process such as the Chevron process or the Phosam-W process (Water Purification Associates, 1977) is required, with concomitantly higher steam consumption.

There is therefore considerable incentive to quantify the steam rates required and to devise improved processes which reduce the steam requirement.

D. Goals of the Present Work

Stripping of aqueous solutions containing combinations of ammonia, carbon dioxide and hydrogen sulfide has been analyzed and studied experimentally (Beychok (1967) Van Krevelen, et al. (1949)). But when other substances, such as non-volatile anions and cations and volatile and/or

ionizable organics (such as phenols and carboxylic acids) are present, the stripping becomes more complex. These complications all occur in process condensates from solid-fuel conversion. This complexity warrants a closer look at the strippability of these waters. In fact, with a few exceptions (Mercer (1978); Verhoff and Choi (1979)), no previous experimental stripping data for these waters have been reported.

The goals of the present work were:

- (1) To carry out experimental stripping studies on condensate waters from the SRC coal liquefaction pilot plant and on the Omega-9 in situ oil shale retorting experiment,
- (2) to compare these results with predictions of existing correlations of vapor-liquid equilibria for the $\text{NH}_3\text{-H}_2\text{S-CO}_2\text{-H}_2\text{O}$ system, and
- (3) to investigate the causes of any apparent anomalies in the stripping behavior of these waters.

Chapter II. Previous Work

A. Van Krevelen, et al.

Refining, steel production, and other industrial processes have produced waste waters that contain ammonia, hydrogen sulfide and/or carbon dioxide. Much work has been done on measurement and correlation of vapor pressures above these waters. Of all this work, the most commonly cited is that of Van Krevelen, et al. (1949).

The work of Van Krevelen, et al., was directed toward aqueous solutions generated by absorption of ammonia, carbon dioxide, and hydrogen sulfide from coal-pyrolysis and coke-oven gas. They measured the vapor pressure of ammonia, carbon dioxide, and hydrogen sulfide above synthetic aqueous solutions by two methods.

The first method (the static method) involves measuring vapor pressure by sampling the equilibrium vapor above a solution in a closed flask and determines the partial pressures of the solutes. The second method (the dynamic method) was to bubble nitrogen slowly through a solution and determine the partial pressures of the ammonia, carbon dioxide and/or hydrogen sulfide in the evolved gas. Both methods yielded the same results within experimental error.

Van Krevelen, et al., developed a model to explain both their data and data generated by previous experimenters. The parameters in this model were derived from experimental data. The model is described as follows.

Aqueous solutions of ammonia, carbon dioxide and hydrogen sulfide contain nine species:



Solving for concentrations of the nine species requires three mass balances,

$$\text{Total ammonia} \quad A = [\text{NH}_3] + [\text{NH}_4^+] + [\text{NH}_2\text{COO}^-] \quad (\text{II-1})$$

$$\text{Total carbon dioxide} \quad C = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{--}] + [\text{NH}_2\text{COO}^-] \quad (\text{II-2})$$

$$\text{Total hydrogen sulfide} \quad S = [\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{--}], \quad (\text{II-3})$$

one charge balance (neglecting the water ionization)

$$[\text{NH}_4^+] = [\text{HCO}_3^-] + [\text{NH}_2\text{COO}^-] + 2[\text{CO}_3^{--}] + [\text{HS}^-] + 2[\text{S}^{--}] \quad (\text{II-4})$$

and five dissociation equilibrium equations:

$$K_1 = \frac{[\text{NH}_4^+][\text{HCO}_3^-]}{[\text{NH}_3][\text{CO}_2]} \quad \text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{HCO}_3^- \quad (\text{II-5})$$

$$K_2 = \frac{[\text{NH}_4^+][\text{CO}_3^{--}]}{[\text{NH}_3][\text{HCO}_3^-]} \quad \text{NH}_3 + \text{HCO}_3^- \rightleftharpoons \text{NH}_4^+ + \text{CO}_3^{--} \quad (\text{II-6})$$

$$K_3 = \frac{[\text{NH}_2][\text{COO}^-]}{[\text{NH}_3][\text{HCO}_3^-]} \quad \text{NH}_3 + \text{HCO}_3^- \rightleftharpoons \text{NH}_2\text{COO}^- + \text{H}_2\text{O} \quad (\text{II-7})$$

$$K_4 = \frac{[\text{NH}_4^+][\text{HS}^-]}{[\text{NH}_3][\text{H}_2\text{S}]} \quad \text{NH}_3 + \text{H}_2\text{S} \rightleftharpoons \text{NH}_4^+ + \text{HS}^- \quad (\text{II-8})$$

$$K_5 = \frac{[\text{NH}_4^+][\text{S}^{--}]}{[\text{NH}_3][\text{HS}^-]} \quad \text{NH}_3 + \text{HS}^- \rightleftharpoons \text{NH}_4^+ + \text{S}^{--} \quad (\text{II-9})$$

Van Krevelen, et al., chose to modify the dissociation equilibrium constant K 's rather than calculate individual activity coefficients. For example, their K_1 (equation (II-5))

is actually $K_1 = \frac{\gamma_{\text{NH}_3} \gamma_{\text{CO}_2}}{\gamma_{\text{NH}_4^+} \gamma_{\text{HCO}_3^-}} K_{1,\text{eq}}$ where $K_{1,\text{eq}}$ is the true equilibrium constant, and so forth. The K_1 "constant" is then determined as a function of ionic strength.

Van Krevelen, et al., worked in the ammonia rich concentration range. In this range, almost all of the carbon dioxide and hydrogen sulfide (<99%) are in dissociated form. The two species, CO_2 and equations (II-5) and (II-8) need not be solved with the other equations. The vapor pressure can be predicted after determining the equilibrium concentrations of the remaining seven species.

The ammonia vapor pressure is calculated as the product of the free molecular ammonia concentration using a simple Henry's Law proportionality.

$$P_{\text{NH}_3} = [\text{NH}_3] H_{\text{NH}_3} \quad (\text{II-12})$$

$$\text{where } H_{\text{NH}_3} = H^\circ_{\text{NH}_3} \times 10^{-0.025[\text{NH}_3]}$$

The ammonia vapor pressure calculation is not affected by ionic strength.

The actual concentrations of $[\text{CO}_2]$ and $[\text{H}_2\text{S}]$ are not calculated. The carbon dioxide vapor pressure is predicted from the equilibrium

$$P_{\text{CO}_2} = \frac{[\text{NH}_4^+][\text{HCO}_3^-]}{[\text{NH}_3] K_1'} \quad (\text{II-10})$$

where K_1' is a combination of the dissociation equilibrium constant K_1 (see eqn (II-5)) and the Henry's Law constant

for carbon dioxide. This K'_1 is a function of ionic strength, as shown in Figure II-1. The hydrogen sulfide vapor pressure is predicted by the equilibrium

$$P_{H_2S} = \frac{[NH_4^+][HS^-]}{[NH_3] K'_4} \quad (II-11)$$

where K'_4 is also a combination of K_4 (see eqn (II-8)) and the Henry's Law constant for hydrogen sulfide and is a function of ionic strength as shown in Figure II-2.

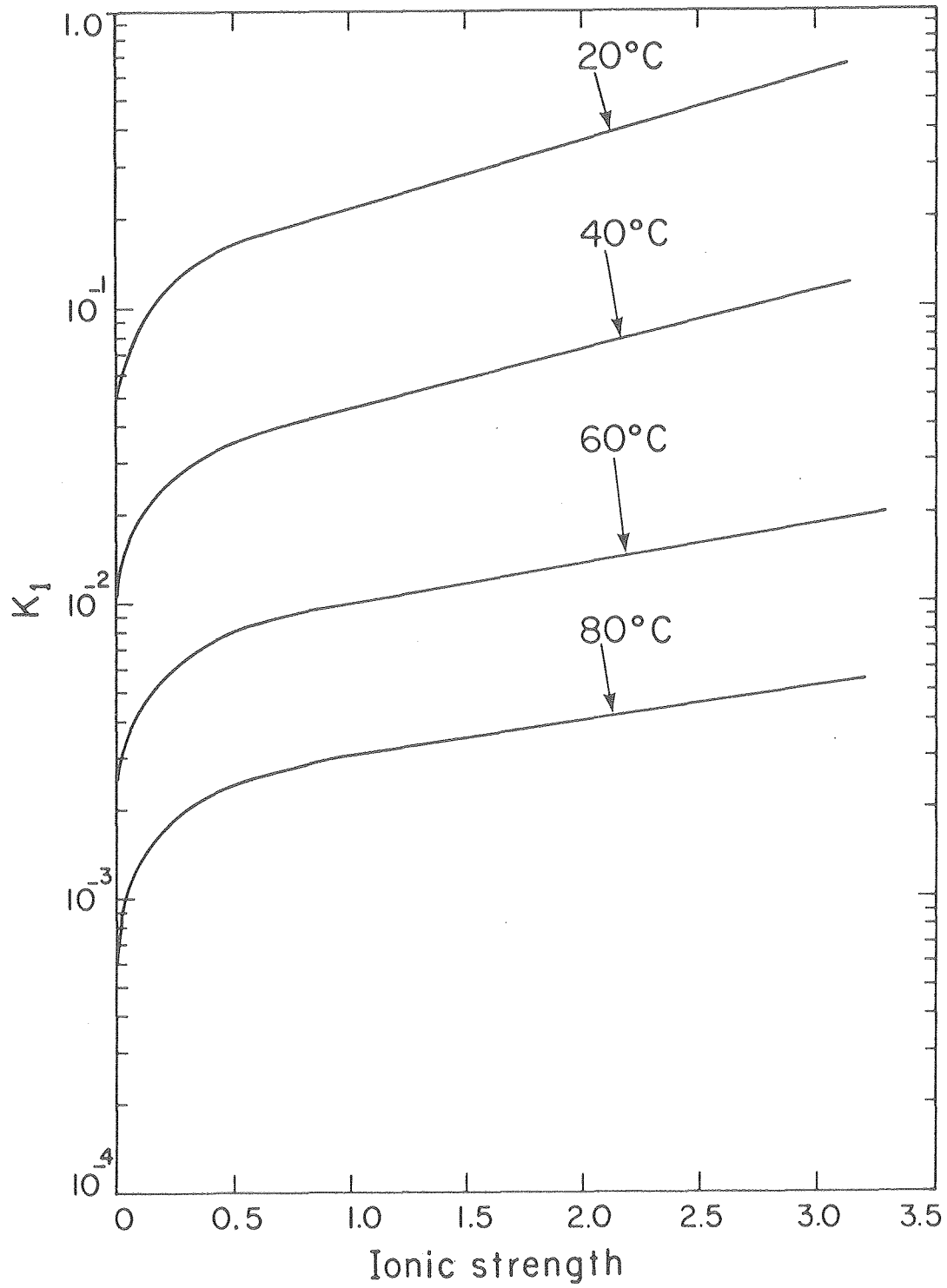
The model of Van Krevelen, et al., worked very well for the concentration range of the data they collected.

B. Edwards, et al., Computer Program

The model of Van Krevelen, et al., worked very well, but covered only a limited range of concentrations. Their model applies only to ammonia-rich systems and solutions of low ionic strength (below 3M). Their model will not apply to very dilute solutions since $[H^+]$ and $[OH^-]$ are not included in their model but $[H^+]$ and $[OH^-]$ contribute to a dilute solution charge balance.

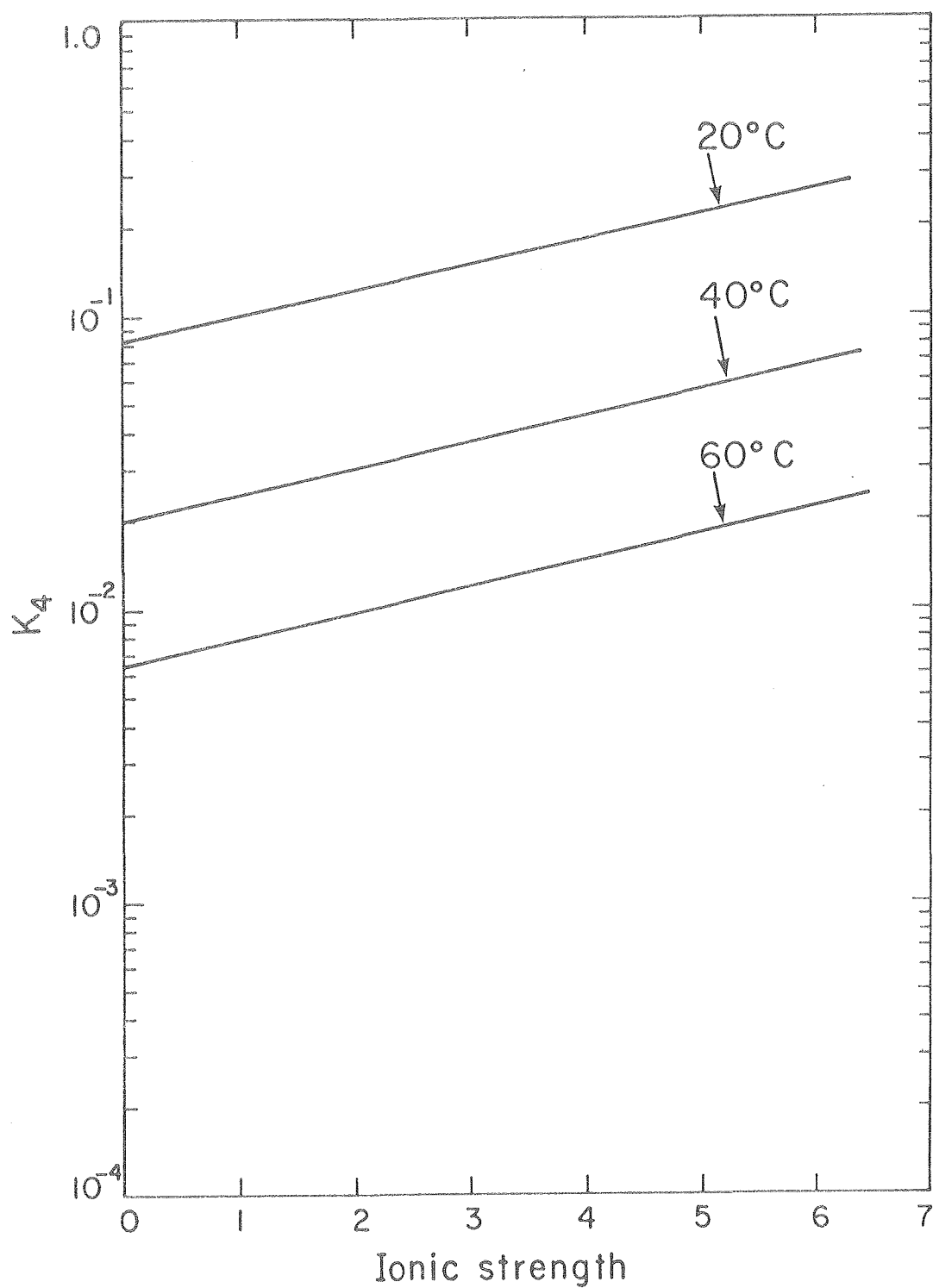
Edwards, et al., (1975), produced a computer program which improved upon the model of Van Krevelen, et al. The program was subsequently upgraded to expand the domain of application (Edwards, et al. (1978)).

This upgraded program, SURFIMP, calculates vapor-liquid equilibria for aqueous solutions containing one or more of



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Figure II-1. K_1^1 variation with ionic strength taken
from Van Krevelen et al. (1949)



XBL 806-1207

Figure II-2. K_4' variation with ionic strength taken
from Van Krevelen et al. (1949)

the following volatile weak electrolytes: NH_3 , CO_2 , H_2S , SO_2 , and HCN . The program may be applied from about 0 to 170°C and for total ionic strength up to about 6 moles per 1,000 Kg water, which corresponds to total concentration between 10 and 20 molal. Since the behavior of the aqueous solution approaches ideality for dilute solutions, there is a lower concentration limit.

SURFIMP calculates vapor-liquid equilibria in a way similar to the Van Krevelen, et al., model. SURFIMP uses an iterative multi-dimensional Newton-Raphson technique to solve simultaneously the equations of mass balance, dissociation equilibria and charge balance, and determines concentrations of all of the species ($[\text{NH}_3]$, $[\text{NH}_4^+]$, $[\text{CO}_2]$, etc.), including $[\text{H}^+]$ and $[\text{OH}^-]$. The vapor pressure of each component is calculated as the product of anionized molecular concentration ($[\text{NH}_3]$, $[\text{CO}_2]$ or $[\text{H}_2\text{S}]$) and an individual Henry's Law constant (similar to the approach for NH_3 in the model of Van Krevelen, et al.).

However, the Van Krevelen, et al., model combined the activity coefficients, dissociation equilibrium, and Henry's Law constants for H_2S and CO_2 into the terms K'_1 and K'_4 respectively. The K' coefficients were taken to be functions of ionic strength.

SURFIMP calculates activity coefficients for each individual species. These activity coefficients are based on ionic strength and on specific ion interactions, as well.

The specific ion interactions are measures of the effect of one particular ion upon another particular ion in solution. The interaction parameters in the program were experimentally determined.

In SURFIMP, interactions of solute species in the liquid phase are described by a form of the equation for activity coefficients of strong electrolytes proposed by Pitzer (1973). Nonidealities in the vapor phase are characterized by fugacity coefficients calculated from an equation of state proposed by Nakamura, Breedveld and Prausnitz (1976).

The program, SURFIMP, is simple to use. The only input requirements are:

- (1) Overall composition, and
- (2) Temperature.

The program calculates:

- (1) Total pressure
- (2) Individual vapor pressures
- (3) pH $(-\log(\gamma_{H^+} \cdot [H^+]))$
- (4) Species concentrations
- (5) Activity coefficients, etc.

which are dependent variables and cannot be used as input to the program. The program assumes that the only ionic species present are the dissociated forms of the volatile weak electrolytes (NH_4^+ , HCO_3^- , HS^- , etc; no Na^+ , Cl^- , $SO_4^{=}$, etc.). The specific ion interactions have been

TABLE II-1

Comparison of Calculations and Van Krevelen, et al., Data

T ^o C	Total Moles/L			Vapor Pressure mmHg								
	NH ₃	CO ₂	H ₂ S	P ^a _{NH₃}	P ^b _{NH₃}	P ^c _{NH₃}	P ^a _{CO₂}	P ^b _{CO₂}	P ^c _{CO₂}	P ^a _{H₂S}	P ^b _{H₂S}	P ^c _{H₂S}
20	0.25	0.127	-	0.94	0.90	0.79	1.45	1.4	1.24			
20	0.50	0.305	-	1.10	1.1	0.93	5.4	5.0	4.21			
20	1.00	0.59	-	1.73	1.9	1.61	7.85	7.5	5.63			
20	1.50	0.75	-	3.72	3.7	3.25	3.8	3.9	2.90			
20	2.00	1.12	-	3.63	3.5	2.93	8.45	9.0	5.97			
20	1.045	0.50	0.045	2.72	2.7	2.39	3.65	3.6	2.66	-	-	-
20	1.09	0.82	0.090	0.57	0.55	0.48	-	-	-	16.91	16.2	14.0
20	1.189	0.41	0.189	4.11	3.8	3.43	1.45	1.8	1.38	3.21	3.6	3.68
20	1.193	0.745	0.193	0.90	0.87	0.79	29.2	32.2	22.4	27.38	22.8	19.8
20	1.39	0.495	0.390	2.42	2.8	2.54	3.70	4.4	3.27	12.56	14.3	13.3

a. Observed.

b. Van Krevelen, et al., modelc. Edwards, et al., computer program

determined only for these ions. A typical SURFIMP output is shown in Figure II-3. A comparison of some of the data of Van Krevelen, et al., calculations from the model of Van Krevelen, et al., and calculations from the program is shown in Table II-1.

Chapter III. Analytical Methods

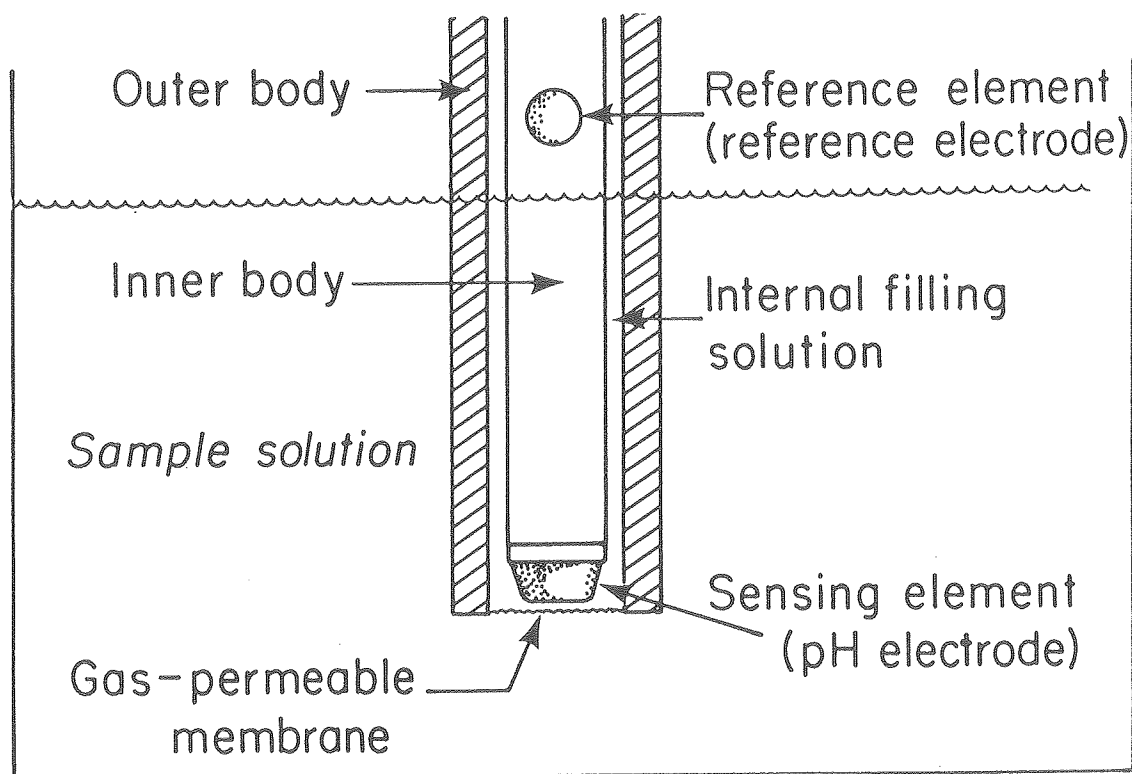
A. Specific Ion Electrodes

Determining aqueous concentrations of ammonia, carbon dioxide and hydrogen sulfide in the presence of each other cannot be easily done. Colorimetric methods will work but are occasionally unreliable and inaccurate and are tedious and time-consuming to perform. A simple, fast, and accurate method of concentration measurement is necessary when many measurements are to be performed.

Recently, Orion Research Inc. developed 'specific ion electrodes' to measure concentrations of dissolved gases and ions in aqueous solution (Orion Research Incorporated Analytical Methods Guide). Measurement with these electrodes is easy, requiring only pH adjustment of the sample. These electrodes are simply placed into the solution and the concentrations are determined from the readings of a millivolt meter. Both gas-sensing and ion-sensing electrodes are available.

The gas-sensing electrodes are constructed as shown in Figure III-1. The outer body and gas-permeable membrane separate the solution being analyzed (sample solution) from the internal filling solution. The inner body is a combination sensing element (pH electrode) and reference element (reference electrode). The reference element senses the constant chloride concentration in the internal filling solution.

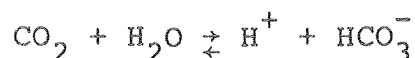
The carbon dioxide electrode (Model No. 95-02 Orion Research Inc.) is a gas-sensing electrode. Total inorganic



XBL 806-1168

Figure III-1. Gas-Sensing Electrode.

carbon concentrations (all forms) are measured by acidification of the sample solution to a pH between 4.8 and 5.2. All of the HCO_3^- and $\text{CO}_3^{=}$ will be converted to molecular CO_2 at this pH. The carbon dioxide desorbs from the sample solution and diffuses as a gas through the gas-permeable into the internal filling solution (see Fig. III-1) until the partial pressures of CO_2 and consequently the CO_2 concentrations are equal on both sides of the membrane. This diffused CO_2 reacts, to a small extent, with the water in the internal filling solution



until equilibrium is reached,

$$K_a = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad . \quad (\text{III-1})$$

The internal filling solution has a high level of sodium bicarbonate so that the bicarbonate can be considered constant and therefore

$$[\text{H}^+] = K'_a [\text{CO}_2] \quad . \quad (\text{III-2})$$

The diffused CO_2 affects the pH of the internal filling solution, and a measure of this pH is thereby also a measure of carbon dioxide concentration. The potential of the pH-sensing element follows the Nernst equation

$$E = E_o - \frac{RT}{ZF} \log [\text{H}^+] \quad (\text{III-3})$$

$$\text{or} \quad E = E_1 - \frac{RT}{ZF} \log [\text{CO}_2] \quad (\text{III-4})$$

Where E = measured potential

E_o, E_1 = reference potential

R = universal gas constant

T = absolute temperature

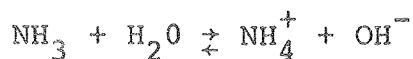
Z = charge (=1 for CO_2 and NH_3)

F = Faraday's constant

and $S = \frac{RT}{ZF}$ = characteristic slope for electrode.

A ten-fold concentration increase of carbon dioxide in the sample solution causes a +59mV change (slope $S = +59\text{mV}$ per decade of concentration) in potential difference for the carbon dioxide electrode at 25°C . The detection limit on carbon dioxide concentration measurements with the electrode is about 10^{-4}M , because carbon dioxide diffuses too slowly across the gas-permeable membrane below 10^{-4}M . The upper limit on carbon dioxide concentration for measurements is 10^{-2}M , since carbon dioxide is rapidly lost from solution above 10^{-2}M ; the solution can, of course, be diluted.

The ammonia electrode (Model No. 95-10 Orion Research Inc.) is also a gas-sensing electrode and is operated similarly to the carbon dioxide electrode. The sample solution must be set to a pH of 11 or greater for ammonia analysis. All of the NH_4^+ in the sample solution is converted to NH_3 in this pH range. The NH_3 diffuses as a gas across the gas-permeable membrane into the internal filling solution. It thereby changes its pH according to the reaction,



with equilibrium

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \quad (\text{III-5})$$

The internal filling solution has a high level of ammonium chloride (NH_4^+Cl^-) so that

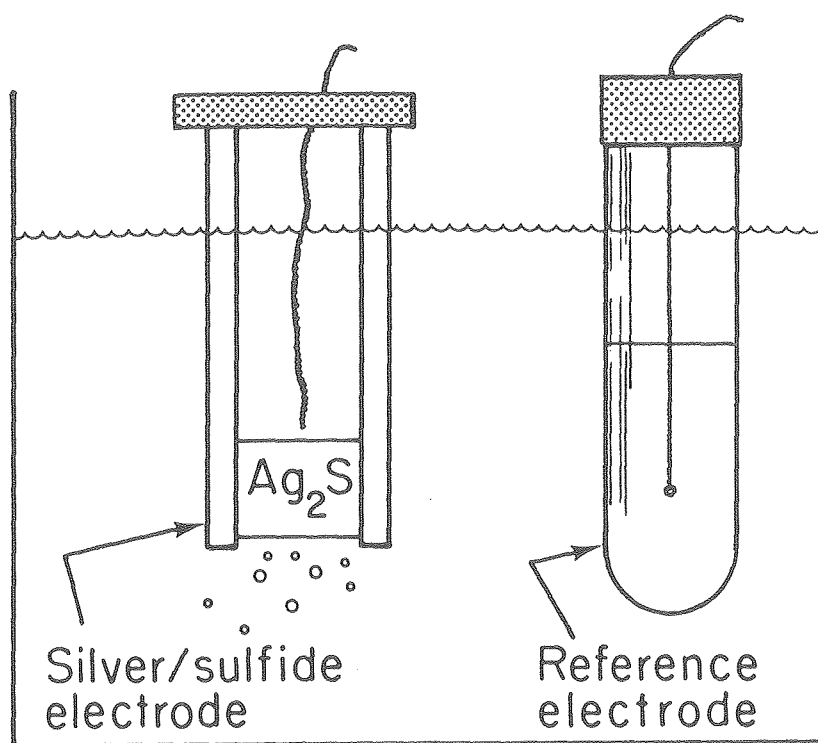
$$[\text{NH}_3] \approx K_b' [\text{OH}^-] \quad (\text{III-6})$$

and measurement of $[\text{OH}^-]$ or $[\text{H}^+]$ (pH) is therefore an indirect way to measure the ammonia concentration.

The ammonia electrode operation is also Nernstian and has a slope of -59mV change per decade ammonia concentration change. The ammonia electrode operates between 10^{-5}M and 1M ammonia sample solution concentration. Samples with higher concentrations can, of course, be diluted.

Carbon dioxide measurement requires the addition of a sodium citrate buffer to adjust the ionic strengths of both standard (calibrating) and sample solutions. This keeps the activity coefficient for carbon dioxide constant in the measured solutions. Ammonia measurement does not require any buffer as the ammonia activity coefficient is not affected much by ionic strength at lower ionic strengths.

Construction of the solid-state, ion-sensing electrode for hydrogen sulfide measurement is shown in Figure III-2. Unlike the gas-sensing electrodes, the sulfide electrode (Model No. 94-16 Orion Research Inc.) measures the concentration of hydrogen sulfide as the dissociated sulfide ion $\text{S}^{=}$ rather than as dissolved hydrogen sulfide gas. The



XBL 806-1170

Figure III-2. Silver/Sulfide, Solid-State,
Ion-Sensing Electrode.

sulfide electrode consists of a chip of silver sulfide bonded into an epoxy body (see Fig. III-2). When this chip is in contact with a solution containing sulfide (or silver) ions a potential develops across the chip. This potential is measured against a constant reference potential (reference electrode), and the measured potential corresponds to the level of sulfide (or silver) in solution as described by the Nernst equation:

$$E = E_0 + \frac{RT}{ZF} \log A$$

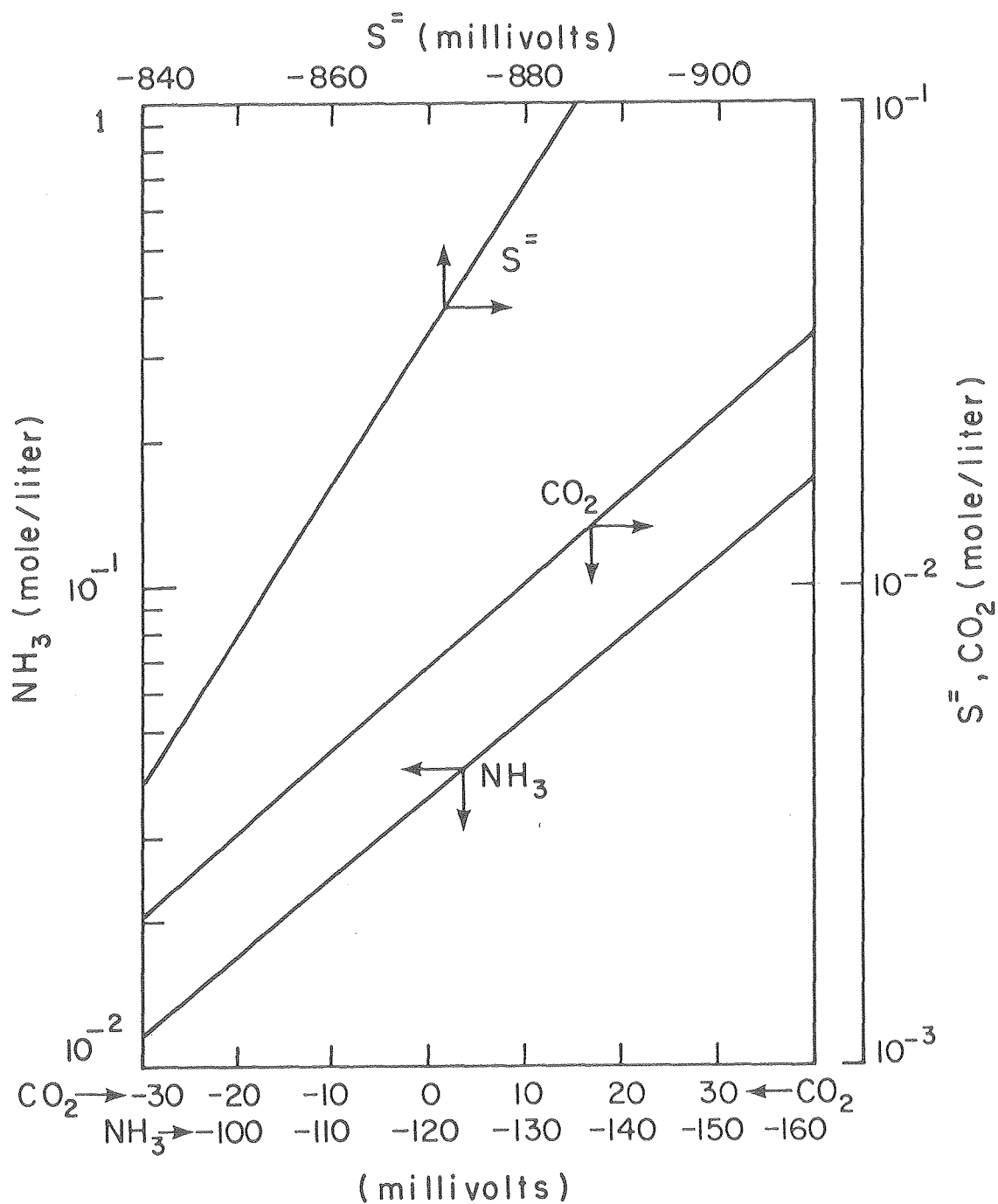
where now $Z = 2$, so that $S = \frac{RT}{ZF} = -29\text{mV/decade}$

and $A = \text{activity of the sulfide ion.}$

An antioxidant buffer is added to the sulfide solution aqueous S^{2-} is otherwise readily oxidized to elemental sulfur. This buffer is added to both standard (calibrating) and sample solutions before measurement to keep the ionic strength constant, thereby keeping the activity coefficient constant. Therefore the activity is proportional to concentration, and a measure of activity is a measure of concentration.

Typical calibration curves for all three electrodes are shown in Fig. III-3. These calibration curves were generated from millivolt measurements of synthetic solutions of known concentrations. From a millivolt reading of the electrode in an unknown sample solution, the concentration can then be determined using the calibration.

Unknown solutions of much higher ionic strength than standard solutions might produce erroneous measurements using typical electrode calibration curves because the



XBL 806-1167

Figure III-3. Typical Electrode Calibration Curves for NH_3 , CO_2 and S^{2-} .

activity coefficients in the unknown solutions could differ from those of standard solutions. The 'known addition' method can produce accurate measurements for those unknown solutions. The 'known addition' method is the addition of a known amount of the species being measured (NH_3CO_2 or $\text{S}^{=}$) to an unknown solution. The unknown concentration can be determined from the difference in potential readings (mV) of the electrode.

For example, 5mL of a known concentration can be added to 200 mL of an unknown solution without changing the ionic strength or activity coefficient appreciably. However, the concentration of the particular species can be changed appreciably, and the potential reading changes. The known addition should change the total concentration by a factor of two to three. The potential difference reading will not change appreciably below a concentration doubling and the activity coefficient might be changed appreciably above a concentration tripling.

$$\text{Before known addition: } E_1 = E_o - S \log C_1$$

$$\text{After known addition: } E_2 = E_o - S \log C_2$$

Where C_1 = unknown concentration

$$C_2 = \frac{C_{\text{std}}V_2 + C_1V_1}{V_1 + V_2}$$

C_{std} = known concentration

V_1 = original volume

V_2 = added volume

Subtracting and rearranging

$$C_1 = \frac{\text{Cstd } V_2}{(V_1 + V_2) 10^{\frac{E_2 - E_1}{S}} - V_1}.$$

The known addition method is simple, fast and reproducibly accurate. This method was used extensively in concentration determinations for the process condensates in the present work.

An excellent alternate method for sulfide analysis is titrating using the sulfide electrode. Since the sulfide is measured in the dissociated state as $S^{=}$, it can be precipitated by heavy-metal ions such as Cu^{+2} or Pb^{+2} . The unknown solution is titrated until the electrode millivolt measurement goes off scale. Addition of Cu^{+2} was used for process condensates since Pb^{+2} will precipitate the CO_2 as $PbCO_3$.

B. Wet Chemistry

Thiosulfate concentration was determined by iodometric titration using 0.1 N I_2 in KF with starch indicator.

Sulfate concentration was determined gravimetrically as barium sulfate, by addition of $BaCl_2$ solution, filtration, drying and weighing.

Chloride concentration was determined by two methods. In the first method, silver nitrate was added to the solution to precipitate the Cl^- as $AgCl$ until free Ag^+ was detected by the silver/sulfide electrode (similar to $S^{=}$ precipitation

with Cu^{+2}). In the second method, excess Ag^+ was added to the solution and the precipitate filtered, dried and weighed. Results of the two methods agreed very well, within 3%.

C. Meter Measurements

The pH of all solutions was measured by a Corning Model 12 pH meter using a Ag/AgCl pH electrode and a standard reference electrode. The millivolt meter section of this Corning pH meter was used in conjunction with the specific-ion electrodes.

The volume of nitrogen stripping gas passed through solutions was measured by a Labline wet test meter (1 ft³ per revolution).

Chapter IV. Apparatus and Procedure

A. Stripping

1. SRC Wastewater.

The apparatus used in stripping the SRC condensate water is shown in Fig. IV-1. A one-liter flask was charged with 500 mL of raw condensate water containing

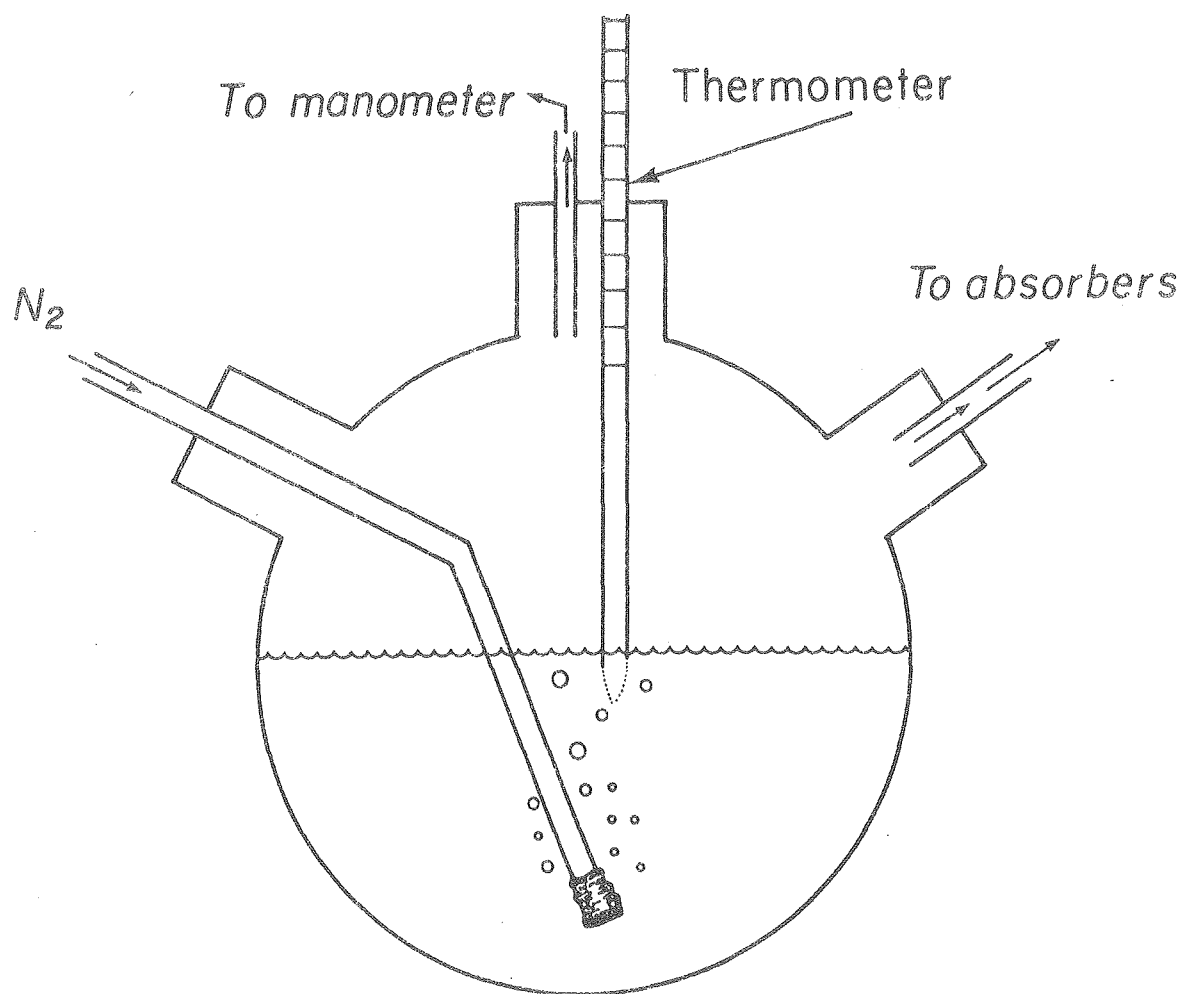
2.95 M NH_3

1.25 M CO_2

0.91 M H_2S

Nitrogen was slowly passed through the solution at about two cubic feet per hour using a fritted bubbler. The condensate water was kept at room temperature (about 20°C). Temperature was measured by means of a thermometer with graduations of 0.1°C. The nitrogen bubbled through about four inches (10 cm) of liquid depth. The total pressure in the stripping flask was approximately 250 mmHg above atmospheric. Pressure was measured by means of a mercury filled U-tube manometer with graduations of 0.1 inch of mercury. Between measurements, 0.3 mL of deaerated distilled water was added per cubic foot of nitrogen passed through the condensate water to replace the water removed with the nitrogen.

The stripping was continued until the vapor pressures of all the solutes dropped below 1 mmHg. At this point, the measured concentrations of the condensate water were:



XBL 806-1166

Figure IV-1. One-Liter Stripping Flask

0.80 M NH_3
 0.22 M CO_2
 5×10^{-5} M H_2S .

Then 250 mL of the solution being stripped was transferred to a 300 mL three-neck heart-shaped flask (see Fig. IV-2). This was to increase the rate of solute depletion by removing a greater per cent of the solutes per cubic foot of nitrogen passed through with a smaller solution volume. The heart-shaped flask had a four-inch liquid height above the fritted bubbler.

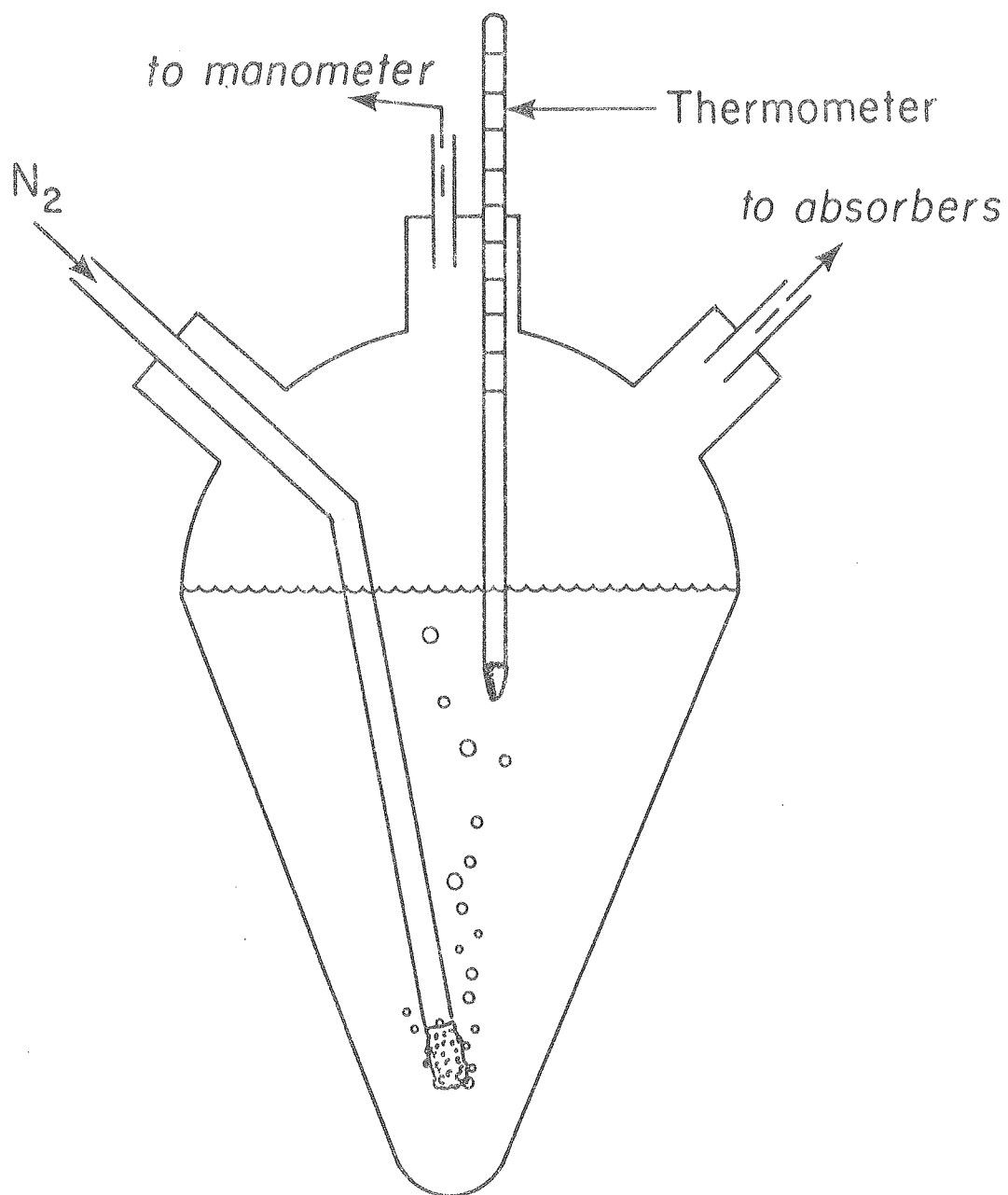
The condensate water darkened upon further stripping, and the vapor pressures dropped rapidly. This water was stripped to final concentrations of

0.53 M NH_3
 0.006 M CO_2
 $<10^{-5}$ M H_2S .

To investigate the possibility that the darkening was due to something in the flask, a separate pre-stripped solution was charged into the heart-shaped flask after thorough cleaning of the flask. This solution was SRC condensate water prestripped by nitrogen at room temperature to concentrations of:

0.75 M NH_3
 0.13 M CO_2
 3×10^{-5} M H_2S

before being placed in the flask. This solution also darkened upon further stripping, and the vapor pressures dropped



XBL 806-1169

Figure IV-2. Heart-Shaped Flask

rapidly. The stripping was continued until the vapor pressures of all the solutes dropped below 0.01 mmHg. The final concentrations in the SRC condensate water were:

0.46 M NH_3

0.002 M CO_2

$<10^{-5}$ M H_2S .

Foaming was a problem in stripping the wastewater. A one-liter, two-neck defoaming flask (see Fig. IV-3) was placed on top of the stripping flask to prevent liquid entrainment into the absorbers. The foam bubbles broke in the defoaming flask, and the liquid drained back into the solution being stripped.

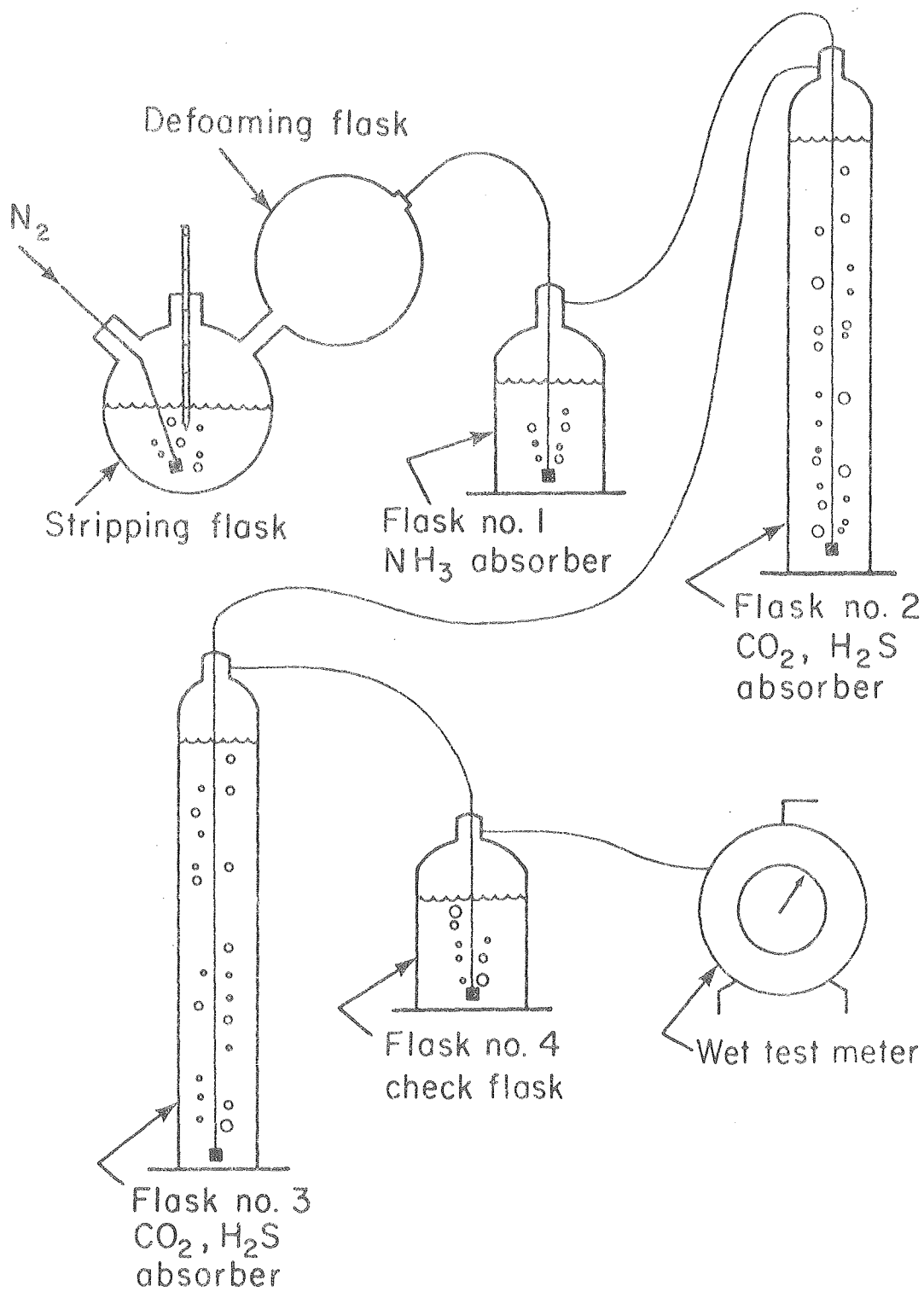
2. Omega 9 Retort Water.

The Omega 9 retort water was stripped in a way similar to that carried out for the SRC condensate water. The heart-shaped flask was charged with 250 mL of the retort water, with measured concentrations equal to

0.29 M CO_2

0.22 M NH_3 .

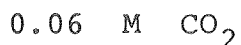
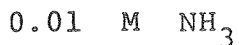
This retort water was stripped with nitrogen at about 2 ft³/hr. with a four-inch liquid height above the fritted bubbler. The nitrogen was presaturated with water for this stripping, so as to eliminate the need for adding distilled water to replace the water stripped out. The temperature was kept near 20°C (room temperature) and the total pressure was about 200 mmHg above atmospheric.



XBL806-1171

Figure IV-3. Bubbling Train

Foaming was also a problem in the retort water, and a defoaming flask was therefore used. The Omega-9 retort water did not discolor during stripping. The measured concentrations were reduced to



before the vapor pressures dropped below 0.01 mmHg.

B. Measurement of Equilibrium Partial Pressures

1. Ammonia.

The absorbing section of the bubbling train is shown in Figure IV-3. The ammonia was absorbed first in Flask #1. The order of absorption is important, as ammonia is very soluble. The acid gases (CO_2 and H_2S) pass through the low-pH ammonia absorber solution.

Flask #1 contained 600 mL of dilute sulfuric acid solution with a six-inch liquid height above a fritted bubbler. The amount of sulfuric acid corresponded stoichiometrically to a change of from 3 to 5% in the ammonia concentration of the condensate water in the stripping flask. Methyl red was used to indicate when that amount of ammonia had been stripped from the condensate water and absorbed in the sulfuric acid solution. The ammonia concentrations in subsequent flasks in the bubbling train (flasks #2 and #3) were measured as a check for incomplete absorption. No ammonia was detected in these flasks by the ammonia electrode. ($<10^{-6} \text{ M } \text{NH}_3$).

2. Carbon Dioxide and Hydrogen Sulfide.

The carbon dioxide and hydrogen sulfide were absorbed

by 1000 mL of dilute sodium hydroxide solutions in each of Flasks #2 and #3 (See Figure IV-3). The liquid height above fritted bubblers in each of the absorbers was 30 inches (75 cm), since the reaction of CO_2 with OH^- is slow enough to require a large interfacial area in order to accomplish the necessary mass transfer. Salt (about 0.1 M NaCl) was added to the absorber solution to increase the interfacial area by decreasing bubble size. The amount of sodium hydroxide in flasks #2 and #3 corresponded stoichiometrically to a 3-5% total acid gas concentration change in the solution being stripped. The majority of the sodium hydroxide was in flask #2.

The final flask in the bubbling train (Flask #4) served as a check for incomplete absorption of the acid gases. It contained a very dilute sodium hydroxide solution at the phenolphthalein endpoint ($\text{pH} \approx 8.3$). If any of the acid gas was not absorbed in flasks #2 and #3, then flask #4 would turn from pink to clear. This occurred only after flasks #2 and/or flask #3 had changed and required only one drop of 1.0 N sodium hydroxide for back-titration.

C. Analysis

When either the methyl red in flask #1 turned yellow or the phenolphthalein in both flasks #2 and #3 turned clear, the nitrogen flow was stopped. The pH of the solution in the flask was measured and the cubic feet of nitrogen was recorded from the wet test meter reading.

The excess sulfuric acid in the ammonia absorber, if any, was back-titrated with sodium hydroxide, and the moles of ammonia stripped were determined. The sodium hydroxide solutions in the acid-gas absorbers were back-titrated with sulfuric acid, and the total acid gas stripped was determined. Samples of flasks #2 and #3 were titrated with Cu^{+2} as CuCl_2 solution (CuS precipitate) using the sulfide electrode to determine stoichiometric equivalence with the amount of hydrogen sulfide in the absorber solutions. The CuCl_2 solution was concentrated enough to precipitate CuS (K_{sp} about 10^{-35}) but dilute enough not to precipitate CuCO_3 (K_{sp} about 10^{-10}). The remainder of the measured total acid-gas uptake was taken to be carbon dioxide. This procedure was repeated for additional intervals of bubbling.

The average vapor pressure of each solute during the absorption interval was determined as

$$P_{\text{NH}_3} = \frac{\text{moles NH}_3}{\text{moles (N}_2\text{+H}_2\text{O)+moles NH}_3\text{+moles CO}_2\text{+moles H}_2\text{S}} \times X$$

X=Total Pressure

with the moles $\text{N}_2\text{+H}_2\text{O}$ determined from the wet-test meter reading and the ideal gas law.

The actual solute concentrations were not measured after every determination of the amounts of gases absorbed. The concentrations in the solutions being stripped were determined by using the measured amounts absorbed in mass balances to interpolate between solution concentration measurements made with the electrodes at regular intervals. If the absorber mass balances were not in agreement with

measured concentrations, concentrations during each absorption interval were calculated by multiplying absorber mass balances by a constant factor to coincide with the measured concentrations. However, the vapor pressures reported were based on the actual measured amount of solutes and were not modified to fit the measured solute concentrations in the stripping flask. The concentrations used in the computer program for prediction of equilibrium partial pressures were the averages of concentrations at the beginning and end of each absorption interval. The pH calculated in the program was compared to the average of the measured pH values at the beginning and end of an absorption interval.

D. Vacuum and High-Temperature Stripping of SRC Condensate Water.

Raw SRC condensate water was stripped at 15 in Hg below atmospheric pressure for five days using nitrogen supplied very slowly (about $0.1 \text{ ft}^3/\text{hr}$) through a fritted bubbler. The stripping flask was not opened during the stripping and the vapor pressures were not measured. This was to prevent oxygen from entering the stripping flask and oxidizing the sulfide to elemental sulfur. Only the final concentrations of the condensate water were measured, using specific-ion electrodes. The pressure was controlled by a vacuum pump and ballast tank which is part of an in-house vacuum system.

Raw SRC condensate water was also stripped at 100°C and one atmosphere total pressure for about three hours using nitrogen supplied through a fritted bubbler at above one cubic foot per hour. Heat was supplied by an electric heating mantle at the rate of about 100 watts using a Variac for control.

The stripping flask was not opened and quantitative vapor pressure measurements were not made during the stripping. The stripping continued until the volatile ammonia was completely removed, as determined by the inability of the stripping gas to change a methyl red solution at the endpoint from red to yellow. Only the final concentrations were measured, using the specific-ion electrodes.

E. Process Condensate Handling and Storage

1. SRC Process Condensate.

The process condensate used in this work was taken from the Pittsburg and Midway Solvent Refined Coal Pilot Plant at Fort Lewis, Washington on December 11, 1979. This condensate was placed in a five-gallon stainless-steel drum and shipped to the University of California at Berkeley on December 12, 1979 at ambient temperature. The condensate shipment arrived on December 13, 1979 and was transferred to dark brown one-gallon bottles and stored at 4°C in a dark storage locker. The condensate water was warmed to room temperature on January 11, 1980, when concentration measurements were taken and the stripping begun.

2. Omega-9 Oil-Shale Retort Water.

The Omega-9 oil-shale retort water used in this work is from the 1976 Rock Springs Site-9 true in situ oil-shale combustion experiment conducted by the Laramie Energy Technology Center (U.S. Dept. of Energy). The retort water was stored at 4°C in thirty-gallon stainless-steel drums at the Lawrence Berkeley Laboratory (Farrier et al; 1977). The retort water was warmed to room temperature on February 27, 1980, when concentration measurements were taken and the stripping begun.

Chapter V. Results and Discussion

A. SRC Condensate Water

1. Data and Explanation.

The SRC condensate water was stripped with nitrogen until the ammonia, carbon dioxide and hydrogen sulfide vapor pressures dropped below 0.01 mmHg. Approximately 450 cubic feet of nitrogen were passed through the 500 mL of condensate water, removing effectively all of the carbon dioxide and hydrogen sulfide. Approximately 0.5M ammonia remained in the solution. The initial condensate water was a yellowish clear liquid, but the stripped water was dark and murky, almost black in color.

Observed results for stripping of 500 mL of the condensate water are shown in Figure V-1. The tabulated values that are represented by Figure V-1 are given in Table B-1. When 250 mL of the condensate was transferred to the smaller heart-shaped flask, after 200 ft³ of nitrogen had been passed through the water, the actual ft³ was multiplied by two for plotting in Figure V-1, in order to keep the same ft³/500 mL for graphical presentation. The stripping beyond 380 ft³ of nitrogen is not shown since the vapor pressures were very low and the solute concentrations were not appreciably changed as the final 70 ft³ of nitrogen passed through the water.

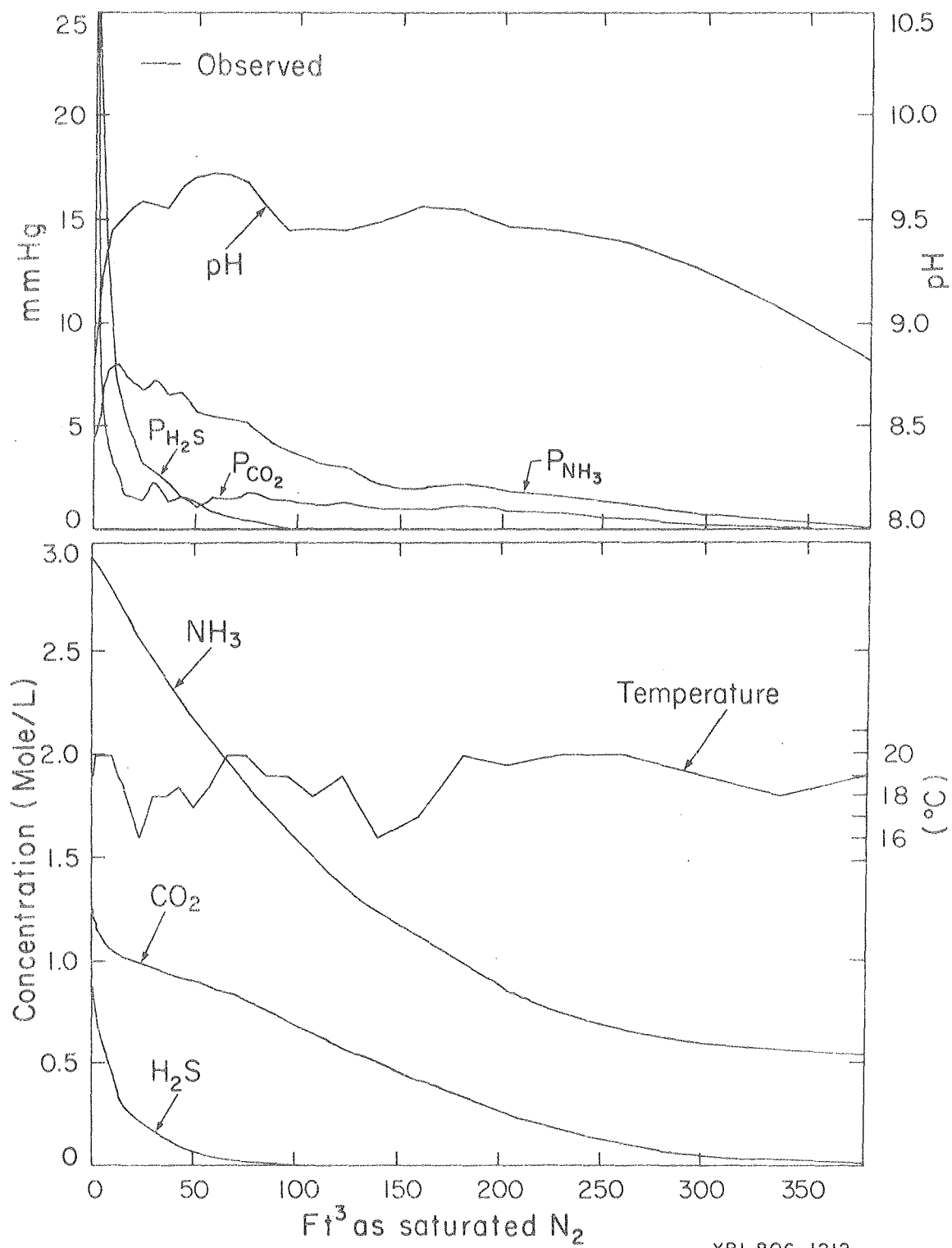


Figure V-1. SRC Condensate Water Stripping

The hydrogen sulfide readily came out of solution; half of it was removed by the first ten ft³ of nitrogen. The carbon dioxide also rapidly evolved from solution initially since both of the acid gases were quite volatile (high vapor pressure) at a pH less than 9.2. The pH increased rapidly with the evolution of the acid gases. The pH stayed between 9.4 and 9.8 for most of the stripping (most of the solute removal). At this higher pH, the ammonia became appreciably volatile, with minor fluctuations in vapor pressure, apparently due to temperature changes. Essentially all of the hydrogen sulfide was removed from the condensate water with the first 100 ft³ of nitrogen.

The ammonia and carbon dioxide were steadily removed from the condensate water, with decreasing vapor pressures of the two accompanying the removal of these solutes. The condensate water darkened after about 200 ft³ of nitrogen had been passed through. The rate of solute removal decreased after the solution darkened. Also, the pH began to decrease upon solution darkening. The first condensate water (shown in Figure V-1) was stripped to 0.53 M NH₃ after about 450 ft³/500 mL had been passed through the water. A second, prestripped condensate water sample, not shown graphically, but tabulated in appendix B-2, was also used because the first water had darkened. This second, pre-stripped sample was stripped to 0.46 M NH₃ after about 750 ft³/500 mL had been passed through the water. Both final stripped condensate waters were very low in carbon dioxide

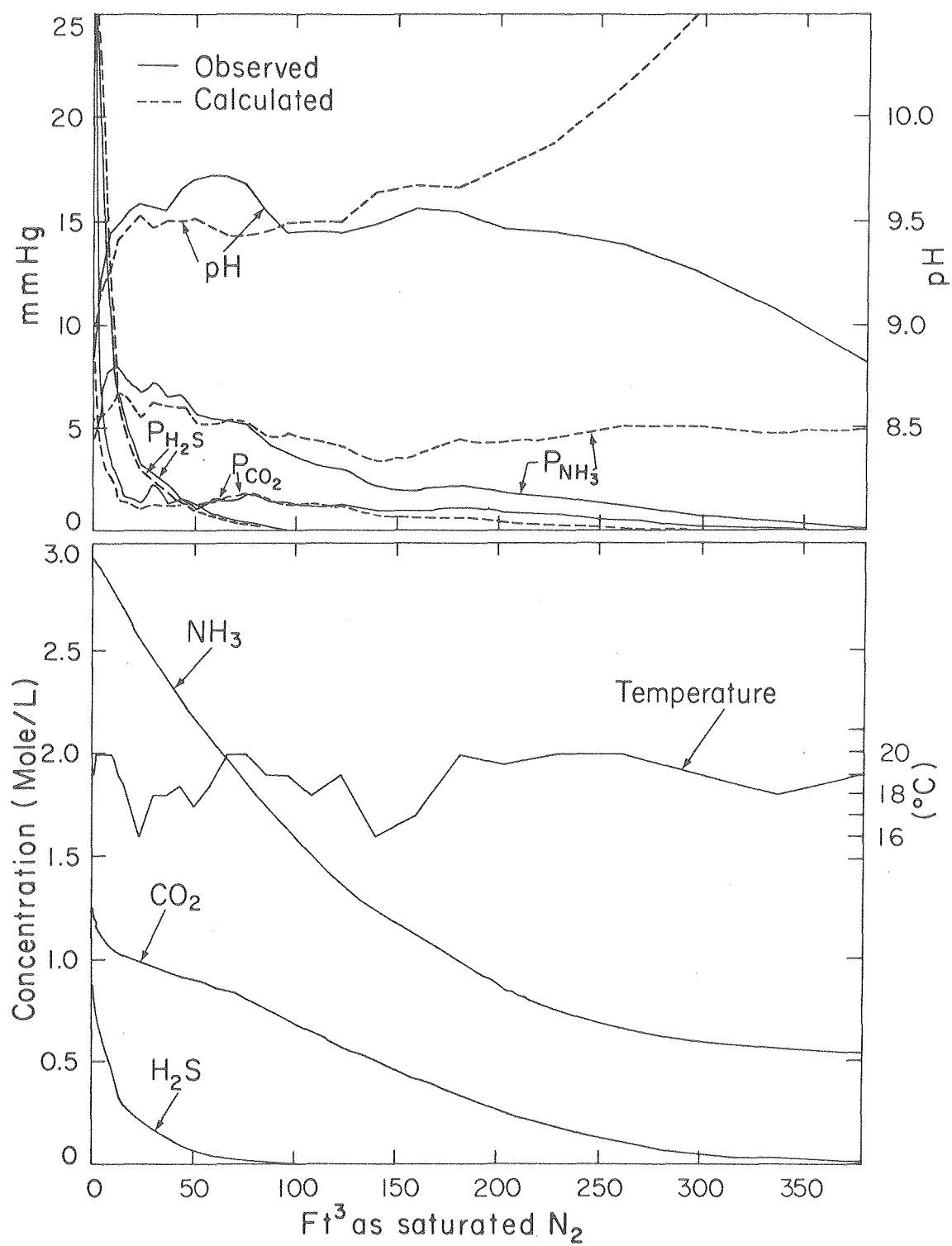
and hydrogen sulfide, below electrode-measurable levels. Both stripped waters darkened after about 200 ft³/500 mL had been passed through the water.

2. Calculations vs. Experimental Results.

The computer program, SURFIMP, was used to calculate vapor pressures for comparison with experimental results, as shown in Figures V-2 and V-3. The vapor pressures and pH were calculated from the corresponding concentrations and temperatures for each bubbling interval, and are plotted against cubic feet of the saturated nitrogen stripping gas as measured by the wet-test meter.

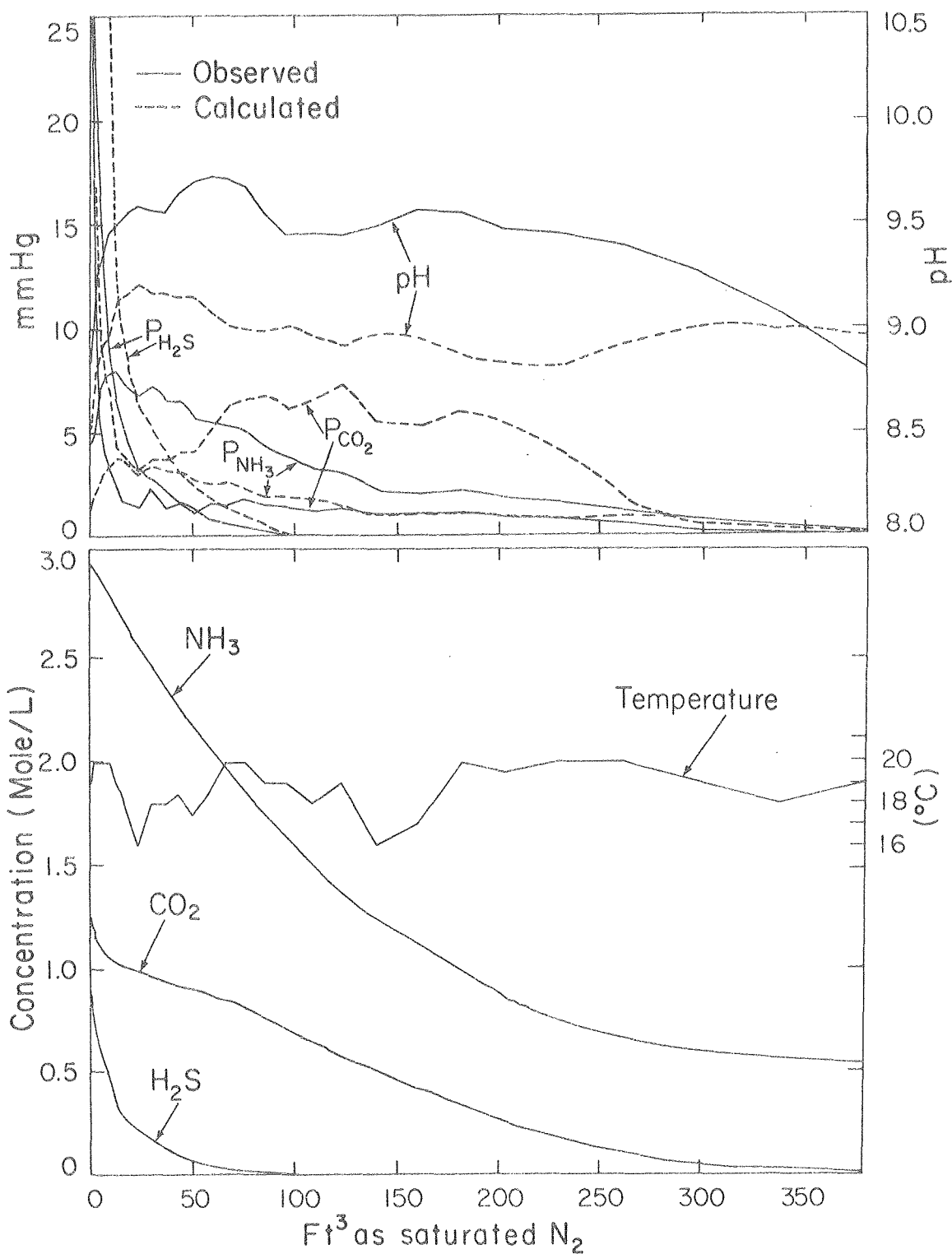
The calculated curves in Figure V-2 are based on only NH₃, CO₂ and H₂S being present in solution. The calculations do not account for any other volatile and/or non-volatile ions that were present in solution.

The predicted vapor pressures of the two acid gases and the predicted pH are in very good agreement with the measured values before the solution darkened at 200 ft³ of saturated nitrogen. The predicted ammonia vapor pressures were fairly close to measured values up to 100 ft³ of stripping gas, but predictions were higher than observed between 100 and 200 ft³ of stripping, presumably due to a calculated pH higher than that measured. When the solution darkened (200 ft³ of N₂), the measured pH began to decrease. But the calculated pH increased due to the richness of ammonia in solution, and the resultant predicted vapor pressures were therefore inaccurate for bubbling intervals beyond 200 ft³ of stripping gas.



XBL 806-1211

Figure V-2. Calculated Comparison with SRC Condensate Stripping. (No excess anions).



XBL 806-1210

Figure V-3. Calculated Comparison with SRC Condensate Water Stripping. (0.45 eq/L excess anions)..

The computer program was modified in an attempt to account for the measured and unknown extra anions present in the solution. An offset of 0.45 N anion concentration was introduced in the charge balance (see equation II-4), along with an additional ionic strength of 0.36 M for the activity coefficient calculations. The specific ion interaction parameters for $\text{S}_2\text{O}_3^{=}$, Cl^- , etc., are not in the program calculations for activity coefficients. Consequently, the results of these calculated results shown in Figure V-3 are just a "good" representation of the effect of the anions on the calculated values.

The calculated pH and vapor pressures shown in Figure V-3 were quite inaccurate for the majority of the bubbling interval measurements. After 300 ft³ of stripping gas had been passed through the condensate water, and beyond, the predicted values were in better agreement with the experimental data. It appears that the extra anions affect the pH and vapor pressures only after the solution darkens. This strongly suggests that most of the anions (sulfate, thiosulfate and the unknown anions) were not formed until after the solution darkened. This is in agreement with the proposed mechanism involving oxidation of sulfur, which is put forward in Sections 3 and 5. This is also in agreement with a decrease in measured pH beyond 200 ft³ (darkened solution) but an increase in calculated pH as shown in Figure V-2, where no additional anions were assumed present.

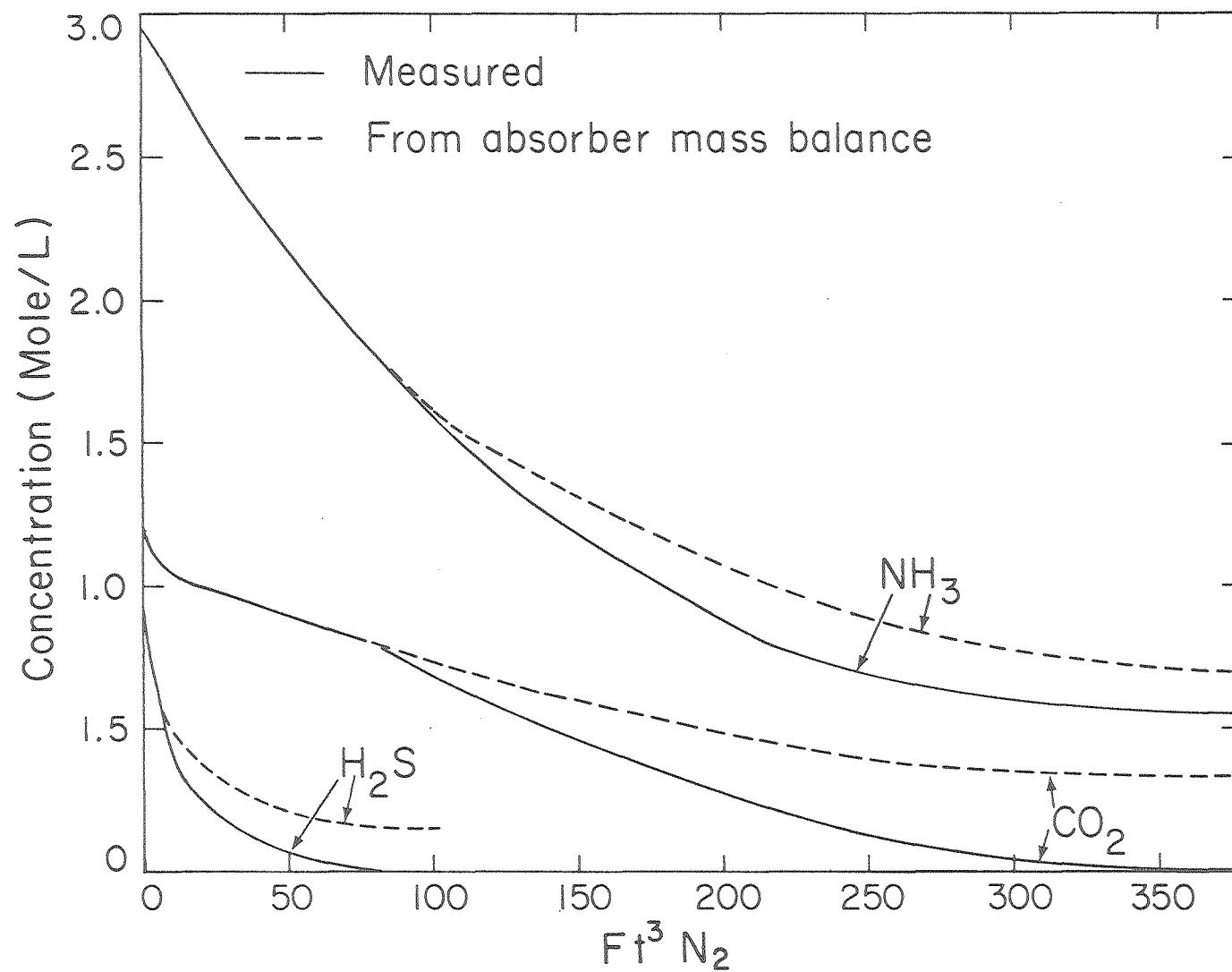
3. System Solute Loss.

The electrode measurements of the solute concentrations made at regular intervals did not agree at all points with the concentrations calculated from absorber mass balances. The flask concentrations for each bubbling interval were determined by multiplying the amount of solute absorbed since the last previous flask concentration measurement by a constant factor, chosen to match the flask concentration at the next measurement. The check flask in the bubbling train (see Figure IV-3) indicated complete absorption of acid gases. Also, no ammonia was detected in the acid gas absorbers. A comparison of absorber mass balances and measured concentrations is shown in Figure V-4 (taken from Appendix B-3).

The overall hydrogen sulfide concentration loss was 0.14M, or 16% of the initial hydrogen sulfide concentration. This hydrogen sulfide seems to have been oxidized to elemental sulfur. Hydrogen sulfide oxidizes in aqueous solutions according to the reaction



There were small yellow particles found on the glassware (stripping flask) that appeared to be elemental sulfur. The oxygen probably got into the flask when it was opened between bubbling intervals to take pH measurements. The nitrogen supply was 99.97% pure, but 0.03% oxygen could also have been a significant source of oxygen when many cubic



XBL 806-1213

Figure V-4. SRC Condensate Water Concentration Comparison.

feet were passed through the water.

The overall carbon dioxide concentration loss was 0.32 M, or 26% of the initial carbon dioxide concentration. This loss became detectable after the hydrogen sulfide had been largely removed from the condensate water. The greatest absolute amount of the apparent loss of carbon dioxide (0.2 M) occurred while the condensate water was still transparent (between 80 and 200 ft³). The greatest relative loss occurred after solution darkening with a measured mass balance disagreement during that time of 50% (or 0.12 M CO₂ loss). A small part of this discrepancy (3-5%) could have been due to experimental error. It seems likely that some of the carbon dioxide was consumed in a reaction, since the absorption of acid gases was complete as indicated by the check flask in the bubbling train. One likely carbon dioxide-consuming reaction is indicated in the next section.

The overall ammonia concentration loss was 0.12 M, or 6% of the initial ammonia concentration. This apparent loss occurred before solution darkening, since the absorber mass balance agreed with the rate of change of measured concentrations beyond 200 ft³ of nitrogen stripping gas, as shown in Figure V-4 by parallel lines. This discrepancy could be due to experimental error, consumption by reaction, or both.

The solution remained transparent as long as there were substantial amounts of sulfide present. After all of

the hydrogen sulfide had been removed, discoloration occurred. This discoloration probably came from oxidation of organic compounds, such as polyhydric phenols. The presence of sulfide may have discouraged this discoloration by preferential oxidation of sulfide to elemental sulfur.

4. Vacuum and High-Temperature Stripping.

The vacuum-stripped SRC condensate water remained a yellowish clear solution after five days of stripping with nitrogen. The amount of nitrogen passed through was not measured. The final measured concentrations and pH were

$$0.38 \text{ M } \text{NH}_3$$

$$0.09 \text{ M } \text{CO}_2$$

$$<10^{-4} \text{ M } \text{H}_2\text{S}$$

$$\text{pH} = 9.75.$$

No elemental sulfur specks were visible on the stripping flask.

After exposure to the atmosphere for a few minutes (to withdraw samples for measurements), the solution was sealed in a flask and stored at room temperature. Within two hours the solution turned dark and murky. The darkened solution contained no measurable carbon dioxide, but the ammonia concentration and pH remained unchanged. Apparently, the carbon dioxide was consumed in an oxidation reaction with the phenolics. The reaction mechanisms for phenol oxidation proposed by Taylor and Battersby (1967) do not include carbon dioxide consumption, but the carbon dioxide did disappear when the phenolics oxidized (solution darkened).

The SRC condensate water stripped at high temperature (100°C) turned dark after thirty minutes of stripping. After three hours, the volume of condensate water had been reduced from 600 mL to 250 mL, and the stripping was stopped. The stripped water contained no measurable carbon dioxide or hydrogen sulfide (below electrode detection) but contained 0.23 M NH_3 in 250 mL or 0.10 M NH_3 , when the final volume was corrected back to 600 mL to account for the water lost due to boiling.

The stripped water was a brownish semi-transparent liquid with a pH of 6.0. The solution contained small black emulsified oily globs that were soluble in acetone. These globs may have been oxidized phenolic products.

5. Anion Concentrations in Condensate Water.

The first SRC process condensate was stripped at room temperature to a final ammonia concentration of 0.53 M NH_3 . The stripped condensate had a pH of 8.2 and had no measurable carbon dioxide or hydrogen sulfide. The ammonia was believed to be paired with non-volatile anions since about 95% of the NH_3 would exist as NH_4^+ at a pH of 8.2.

The measured concentrations of anions in the stripped condensate water were,

$$0.12 \text{ M } \text{S}_2\text{O}_3^{=}$$

$$0.06 \text{ M } \text{Cl}^-$$

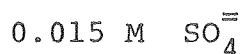
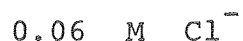
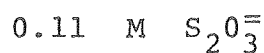
$$0.015 \text{ M } \text{SO}_4^{=}$$

which would pair with 0.33 M NH_4^+ . This left 0.17 M NH_4^+ (95% of 0.53 M, less 0.33 M), plus or minus experimental error,

apparently paired with an unknown anion.

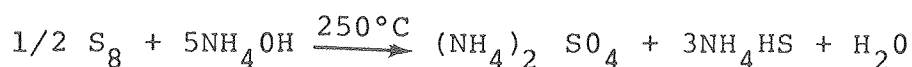
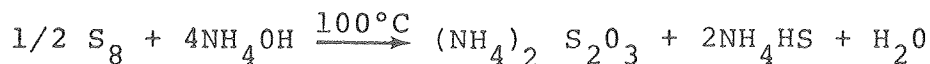
The pre-stripped condensate water, used because the first solution darkened, was stripped to an ammonia concentration of 0.46 M. The final pH of this stripped condensate was 7.5, with no measurable carbon dioxide and hydrogen sulfide present. About 99% of the NH_3 would exist as NH_4^+ at a pH of 7.5.

The measured equivalence of anions in the stripped condensate were,



which would pair with 0.31 M NH_4^+ . The remaining 0.15 M NH_4^+ , plus or minus experimental error, was apparently paired with an unknown anion.

The initial thiosulfate concentration in the raw SRC condensate was 0.01 M $\text{S}_2\text{O}_3^{=}$. The initial sulfate concentration was less than 0.001 M $\text{SO}_4^{=}$. The final concentrations of these two species determined in the stripped waters showed an apparent increase. The elemental sulfur (specks found on glassware) was probably oxidized further according to the reactions outlined by Pryor (1962):



The temperature in the stripping flask (about 20°C) was well below the temperature indicated by Pryor for these reactions to occur, but it should be recognized that much time (4 weeks)

was allowed during the stripping. Also, there may have been trace elements in the water that acted as catalysts.

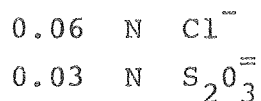
The vacuum-stripped condensate water was not opened during stripping, and no elemental sulfur specks were observed on the stripping flask. Apparently, there was also no thiosulfate created during the vacuum stripping, since the initial and final thiosulfate concentrations were both measured as $0.01 \text{ M S}_2\text{O}_3^{=}$.

The vacuum-stripped condensate water showed a carbon dioxide loss from the water upon solution darkening but the pH and ammonia concentration did not change. The carbon dioxide could have been consumed in a reaction in such a way as to form an ionized functional group, possibly



This possibility was not investigated.

The high-temperature stripped condensate had no measurable carbon dioxide or hydrogen sulfide. This stripped condensate had 0.10 M NH_3 (corrected to initial volume) remaining in solution, with a pH of 6.0. The measured anions that would have paired with the NH_4^+ (all NH_3 in solution is ionized at pH of 6.0) were,



which would pair with about 0.12 M NH_4^+ . It appears that there were no substantial amounts of additional anions in the high-temperature stripped condensate water (100°C).

The unknown anions in the room-temperature stripped condensate water were removed by high-temperature stripping, and/or were not formed under those conditions. These anions also dissociated at a pH as low as 7.5. The unknown anions could not be phenol or resorcinol since their pK values are 9.9 and 9.8, respectively (Kortum, et al., 1961) and essentially none of these two would be dissociated at a pH of 8.2 (or 7.5). The residual ammonia in the stripped water may have been paired with 0.15-0.20 N of somewhat volatile ionized organic constituents, with a pK of 6 or less.

One likely organic constituent found in those waters is acetic acid. Ho, et al., (1976) reports acetic acid concentrations in a coal liquefaction process condensate at about 0.01 M (600 ppm). White (1978) has found concentrations of acetic acid up to 0.16 M (10,000 ppm), but this analysis includes carbon disulfide in the same gas chromatograph peak. Mohr (1980) estimates the acetic acid concentration to be roughly 0.03 M (2,000 ppm) in the SRC process condensate for this work, but an exact acetic acid analysis has yet to be performed.

B. Omega 9 Retort Water

1. Data and Explanation

The Omega 9 retort water was stripped to final concentrations of

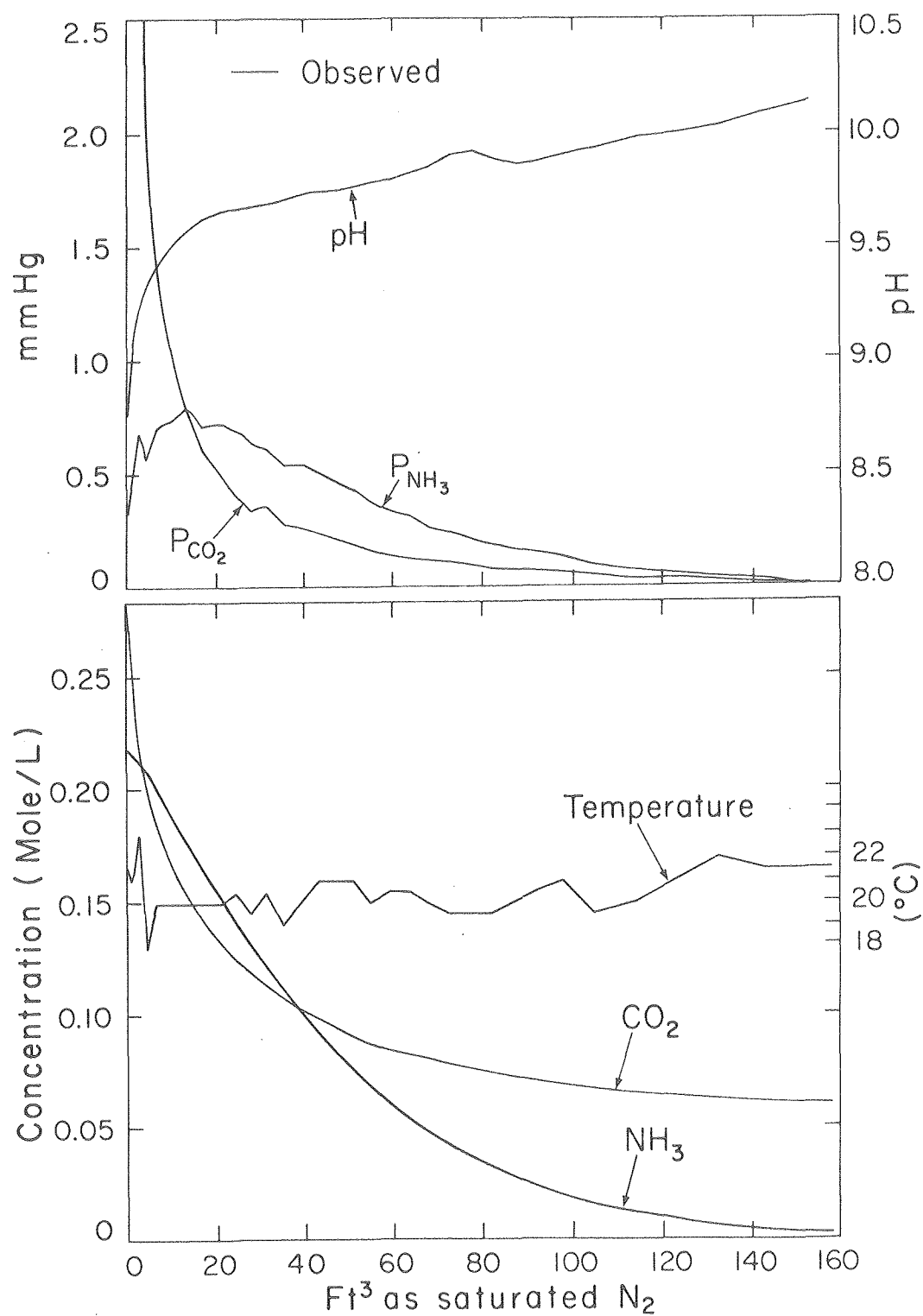
0.002 M NH_3

0.06 M CO_2 ,

and the vapor pressures of these volatile solutes dropped below 0.01 mmHg. About 150 cubic feet of nitrogen had been passed through the 250 mL of retort water. The measured pH values of fresh and stripped retort water were 8.62 and 10.18, respectively. The retort water did not discolor upon exposure to air. Presumably this is attributable to the absence of polyhydric phenols.

The stripping of 250 mL of retort water proceeded as shown in Figure V-5. The carbon dioxide was quite volatile initially, until enough of it was removed to cause a significant increase in pH. With an increase in pH, the ammonia became appreciably volatile and the measured ammonia vapor pressure increased to 0.8 mmHg before declining as the ammonia concentration lowered. After about 25 ft³ of nitrogen had been passed through the solution, the ammonia and carbon dioxide were removed at a fairly steady rate. The pH also increased at a steady rate with a minor fluctuation at about 80 ft³. The reason for this pH fluctuation is not known.

The stripping removed 99% of the ammonia and 80% of the carbon dioxide. The remaining 0.06 M carbon dioxide was



XBL 806-1206

Figure V-5. Omega-9 Retort Water Stripping.

believed to be paired with a previously measured surplus of 0.07 eq/L cations (see Table I-2), and should have existed in solution in the form of HCO_3^- and $\text{CO}_3^{=}$.

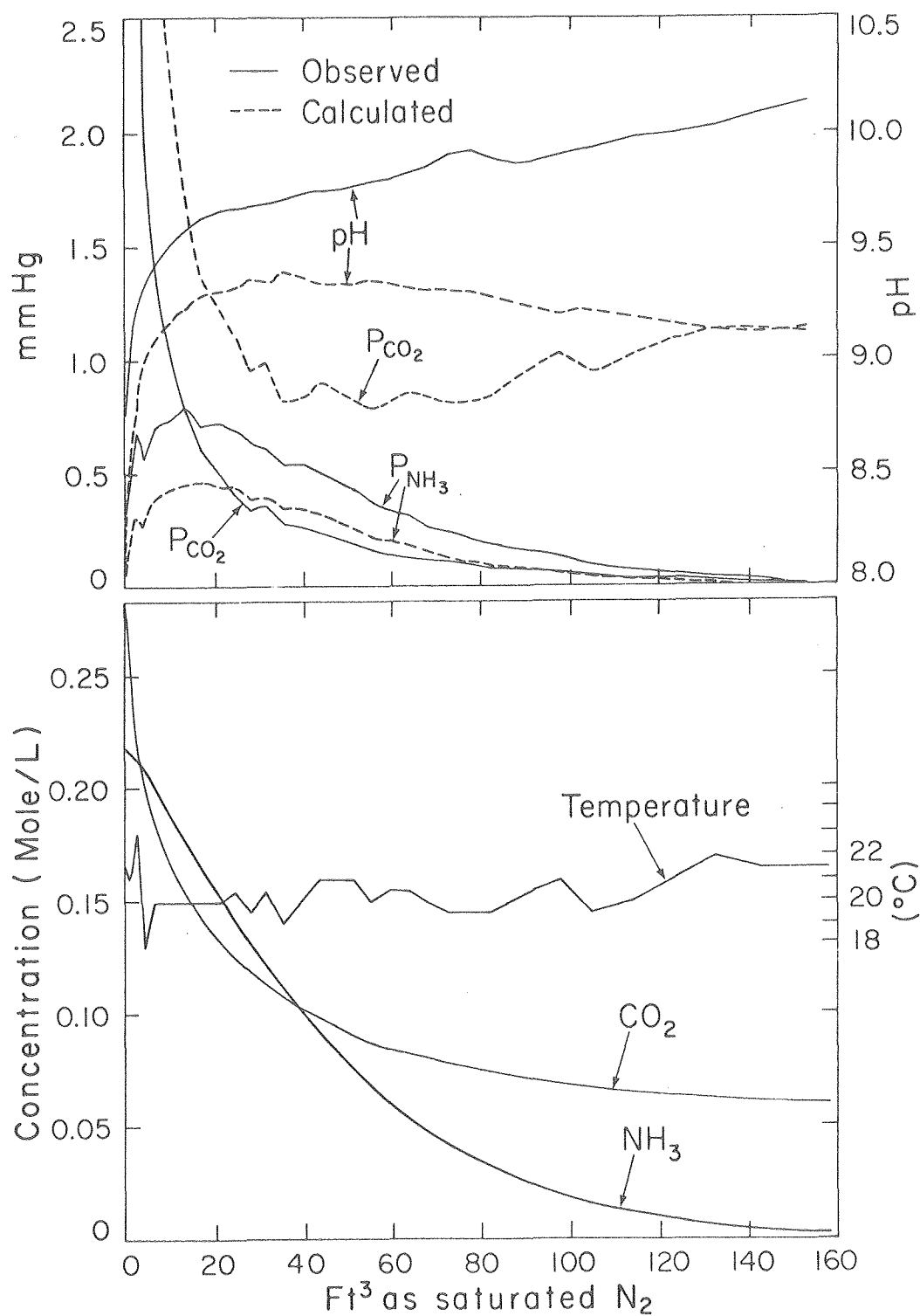
The absorber mass balances were in excellent agreement with the measured concentrations. The discrepancies in overall mass balances for ammonia and carbon dioxide were 2% and 3%, respectively.

2. Calculations vs Experimental Results

The computer program, SURFIMP, was used to calculate the pH and vapor pressures for the measured concentrations and temperatures. The results of the calculations are plotted along with the experimental results against cubic feet of saturated nitrogen stripping gas in Figures V-6 and V-7.

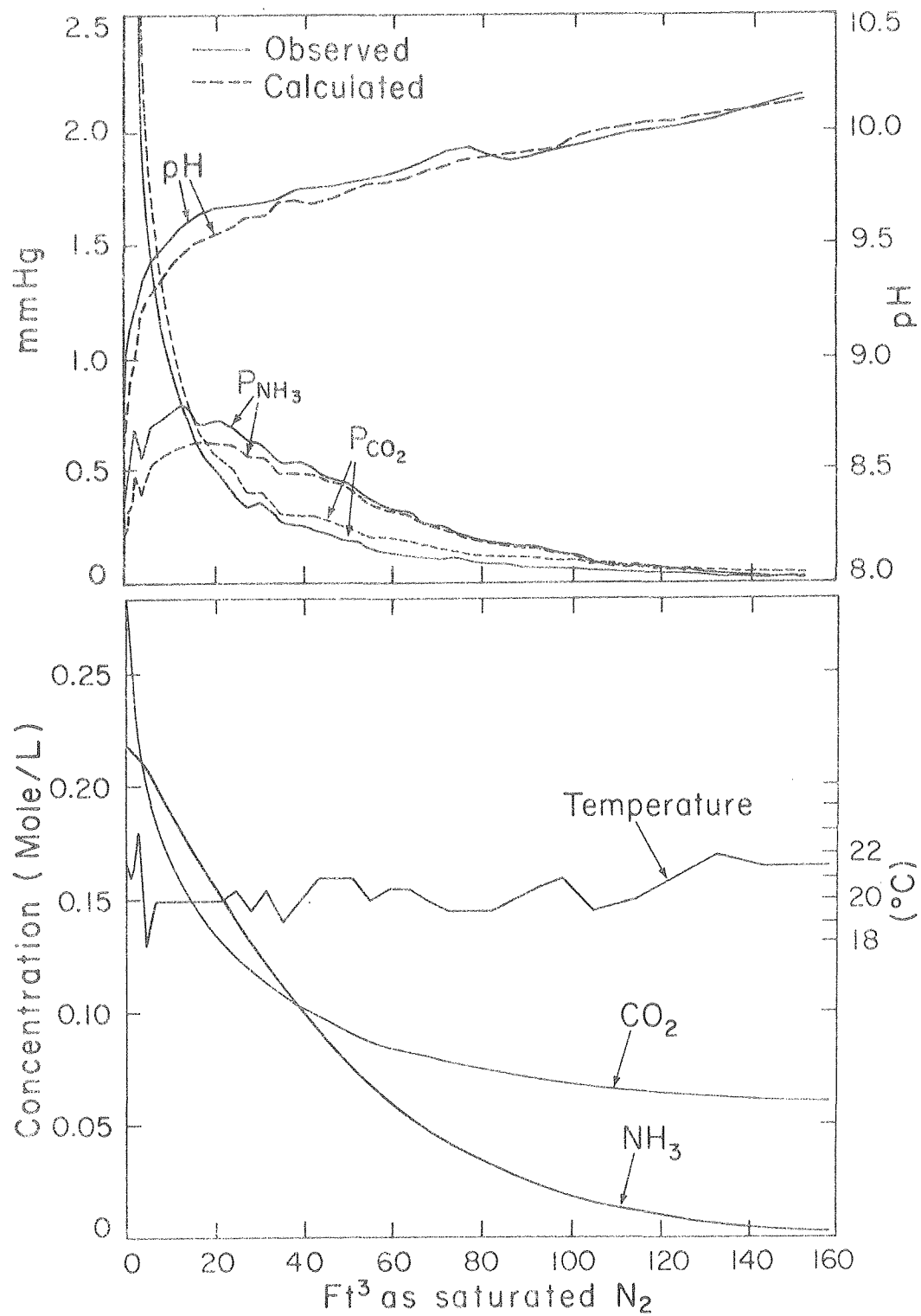
The Omega 9 retort water contained approximately 0.19 eq/l of non volatile cations and 0.12 eq/L of non-volatile anions (see Table I-2). The charge balance in SURFIMP was offset by 0.07 eq/L to account for the surplus non-volatile cations not taken into account in equation II-4. The ionic strength in the program (used to calculate activity coefficients) was increased by 0.204 M to account for the non-volatile ions in the retort water. The results of these calculations are shown in Figures V-6. The specific ion interaction parameters for Na^+ , $\text{S}_2\text{O}_3^{=}$, etc. are not in the program calculations for activity coefficients so the results are just a "good" approximation of the effect of these ions.

The calculated pH and vapor pressures were not in good



XBL 806-1209

Figure V-6. Calculated Comparison with Omega-9 Retort Water Stripping (0.07 eq/L excess cations).



XBL 806-1205

Figure V-7. Calculated Comparison with Omega-9 Retort Water Stripping (0.105 eq/L excess cations).

agreement with the experimental values. The calculated pH showed a decrease near the end of the stripping, whereas the observed pH continuously increased. The calculated carbon dioxide vapor pressure was much higher than that observed, and the calculated ammonia vapor pressure was considerably lower than that observed. These results are in line with the calculated pH being lower than the observed pH.

The charge balance was further adjusted to calculate pH values closer to that of the pH values measured. Results for a charge-balance offset of 0.105 eq/L cations and an additional ionic strength of 0.204 M are shown in Figure V-7.

The calculated pH and vapor pressures for these conditions were in very good agreement with the observed values. Initially the calculated pH was slightly lower than that observed, and the lower calculated ammonia and higher calculated carbon dioxide vapor pressures correspond to this lower calculated pH. When the calculated pH becomes closer to the observed pH (25 ft³ and beyond), the calculated vapor pressures were in excellent agreement with observed values.

The reported measured cation surplus in the retort water was 0.07 eq/L (Table I-2), but the best calculated agreement with experimental values occurred when a cation surplus of 0.105 eq/L was used in the program. The retort water appeared to have 0.035 eq/L of surplus cations not accounted for in Table I-2. This could be due to underestimation of ammonia concentration, over estimation of the carbon dioxide

concentration, inaccurate calculation of activity coefficients in the program, ionizable organic nitrogen compounds not accounted for in analysis (Farrier, et al., 1979), or combinations of the four.

A close look at the stripped retort water characteristics can determine which of these factors contributed to the cation surplus discrepancy. The final ammonia concentration was very low (0.002 M) and with K_b of 1.8×10^{-5} (at 20°C) and pH of 10.15, only 10% of this NH_3 would exist as the cation NH_4^+ . Therefore ammonia concentration underestimation (a few %) is not a contributing factor late in the stripping.

With $K_{a,2}$ of 5.6×10^{-11} (at 20°C) and pH of 10.15, the 0.06 M CO_2 would exist as 0.03 M HCO_3^- and 0.03 M $\text{CO}_3^{=}$ (neglecting activity coefficients). This 0.09 N anion concentration exceeds the reported 0.07 N reported non-volatile cation surplus and is closer to the 0.105 N cation surplus which yielded a better agreement between observed results and program calculations. The computer program calculated the 0.06 M CO_2 to exist as 0.02 M HCO_3^- and 0.04 M $\text{CO}_3^{=}$ (total of 0.10 N anions) with a calculated pH of 10.13 (measured pH of 10.15) using 0.105 N cation surplus whereas the calculated pH was 9.13 using only 0.07 N cation surplus to the charge balance. The calculated activity coefficients for H^+ , HCO_3^- and $\text{CO}_3^{=}$ were 0.64, 0.63 and 0.16, respectively (for 0.105 N cation surplus). The overestimation of carbon dioxide concentration and inaccuracy of activity coefficients

could both be factors in the missing cation surplus, but neither one can be singled out as a factor.

Organic nitrogen compounds in concentrations ranging from 0.01 to 0.045 M (148 to 630 ppm as N) are also reported by Farrier, et al., (1979). Compounds such as alkyl amines (which were not analyzed for), with K_b values of about 3.4, could account for these additional surplus cations. The electrical neutrality of the retort water reported by Farrier, et al., (1979) shows 0.015 N cations unaccounted for in the charge balance.

Chapter VI. Process Ramifications

A. SRC Condensate Water

Removal of all of the carbon dioxide and hydrogen sulfide from the SRC condensate water can be accomplished by batch stripping. Equivalent removals should be achieved by continuous counter-current stripping. The hydrogen sulfide was readily removed from the condensate water, even at room temperature. The carbon dioxide would require a greater boilup rate than for the hydrogen sulfide to be removed in practice, since it is almost all ionized or tied up as NH_2COO^- .

The majority of the ammonia can be removed from the SRC condensate water by stripping. There will be ammonia remaining in a stripped water as NH_4^+ , which will be paired with nonvolatile anions and/or volatile anions not removed by stripping. Removal of this remaining ammonia will require addition of some inexpensive base, such as $\text{Ca}(\text{OH})_2$ or Na_2CO_3 , at later stages in the stripping.

The Edwards, et al., computer program, SURFIMP, can be applied to predict the behavior of the SRC condensate water. The program calculations were good representations of the vapor pressures when the calculated pH values were in good agreement with the measured pH values. In the present work the charge balance was modified for calculations of the vapor pressures and pH values, but gave accurate predictions only late in the stripping when some of the anions ($\text{S}_2\text{O}_3^{=}$ + $\text{SO}_4^{=}$) are believed to have been produced.

Removal of ammonia from these waters is more difficult than removal of the acid gases since the ammonia is much more soluble. Ammonia removal boilup requirements are much higher than those for acid-gas removal. Verhoff and Choi (1979) show that a boilup of about 18% (1.5 lb steam/gallon water feed) is required to reduce ammonia concentration from 50,000 ppm (similar to the concentration of SRC condensate) to 240 ppm using 6 equilibrium stages. This outlet concentration neglects the presence of non-volatile anions.

The energy requirements for stripping of SRC process condensates will be quite high. For example, stripping a 1000 gal/min process condensate from a 3×10^{11} Btu/day SRC plant at a 15% boilup would require about 0.6% of the SRC product energy for stripping steam alone! The high energy requirement for processing these condensate waters warrants a search for new processing technologies to reduce the energy requirement for water treatment.

B. Omega-9 Retort Water

Complete removal of ammonia from the Omega-9 retort water can be accomplished by stripping. There will be carbon dioxide remaining in the stripped water, paired with an excess of non-volatile cations. The final pH of the retort water will be greater than 10, due to this excess of non-volatile cations.

The computer program, SURFIMP, gave a very good representation of the retort water behavior when the charge

balance in the program was adjusted to yield a calculated pH in agreement with the measured pH. The program predictions would probably be even more accurate if the specific ion interaction parameters for the non-volatile ions present in the water were determined and applied to calculations of activity coefficients in the program.

The retort water will require a much lower boilup ratio than the SRC condensate water since the solute concentrations are lower. Also, the ammonia removal (ammonia is the most difficult volatile solute to strip out of water) is aided by an excess of non-volatile cations. Mercer (1978) reports 90% ammonia removal from retort waters similar in composition to those from the Omega-9 test with a boilup ratio of 4.5%, and over 99% ammonia removal with a boilup of 5.3%. The stripped Omega-9 retort water contains a high salt concentration, which may well result in fouling and scaling of process equipment, as well as an additional processing burden to allow water release.

Appendix A

Solute Concentration Calculation

When the measured concentrations did not agree with the concentrations calculated from absorber mass balances, the flask concentrations for each bubbling interval were determined by multiplying the amount of solute absorbed since the last previous flask concentration measurement by a constant factor, chosen to match the flask concentration at the next measurement. For example, consider an initial measured solute concentration of 2.0 M with a one liter volume and a measured solute concentration of 1.5 M after five bubbling intervals as shown in Table A-1. The constant factor for those bubbling intervals is,
$$\frac{\text{moles removed as determined by measured concentration}}{\text{moles absorbed since last concentration measurement}} = \frac{0.5}{0.4} = 1.25,$$
 since the amount of solute absorbed since the last concentration measurement is 0.4 M.

This procedure was used when the measured concentrations and absorber mass balances agreed with a constant factor of 1.0. This method was used as a kind of interpretation to determine concentrations.

TABLE A-1

Sample Concentration Calculation

<u>End of Bubbling Interval No.</u>	<u>Moles Absorbed</u>	<u>Concentrations From Absorber Mass Balance</u>	<u>Constant Factor</u>	<u>Modified Absorbed Moles</u>	<u>Corrected Concentrations</u>	<u>Measured Concentrations</u>
	0	2.00M	1.25	0	2.00M	2.00M
1	0.12	1.88	1.25	0.15	1.85	-
2	0.10	1.78	1.25	0.125	1.725	-
3	0.08	1.70	1.25	0.10	1.625	-
4	0.06	1.64	1.25	0.075	1.55	-
5	0.04	1.60	1.25	0.05	1.50	1.50

Appendix B

SRC Process Condensate Stripping Data

The stripping data of SRC Process Condensate is shown in Tables B-1 through B-5. Tables B-1 and B-2 are data for the stripping of the first process condensate. Tables B-3 and B-4 are data for stripping of the second, prestripped condensate. Tables B-1 and B-3 are comparisons of experimental data and calculated values based on only $\text{NH}_3\text{-CO}_2\text{-H}_2\text{S-H}_2\text{O}$ present in the water. Tables B-2 and B-4 are comparisons of experimental data and calculated values based on 0.45 N excess anions and 0.36 M additional ionic strength. The cubic feet passed through are based on 500 ml of solution ($\text{ft}^3/500 \text{ ml}$). The amounts of cubic feet passed through, concentrations, vapor pressures and pH values are the averages of the values at the beginning and end of bubbling intervals.

Table B-5 is a comparison of the measured concentrations and the concentrations calculated from absorber mass balances alone using the initial concentration as a starting point. Table B-5 is a representation of the stripping of the first SRC condensate water. The amounts of cubic feet passed through and concentrations are the values at the beginning and end of bubbling intervals.

TABLE B-1
SRC Process Condensate Stripping (500mL)

ft ³ N ₂ ^a	T°C	Concentration Moles/Liter			Vapor pressure mm Hg						pH	
		NH ₃	CO ₂	H ₂ S	P _{NH₃}		P _{CO₂}		P _{H₂S}		exp.	calc. ^b
					exp.	calc. ^b	exp.	calc. ^b	exp.	calc. ^b		
0.35	19	2.95	1.23	0.87	4.6	2.8	25.2	9.3	43.6	50.4	8.84	8.92
1.26	20	2.94	1.18	0.80	4.9	3.7	20.8	6.8	27.0	37.3	8.97	9.00
2.67	20	2.92	1.14	0.72	5.6	4.5	9.8	4.9	21.3	26.8	9.13	9.09
4.54	20	2.89	1.11	0.63	7.0	5.1	5.8	3.8	17.8	19.6	9.28	9.17
6.82	20	2.86	1.08	0.56	7.7	5.8	4.2	2.9	12.4	14.7	9.39	9.24
9.54	20	2.81	1.06	0.49	7.9	6.1	3.2	2.5	9.1	11.7	9.47	9.28
12.43	19	2.76	1.04	0.35	8.0	6.7	2.5	1.6	6.7	6.3	9.50	9.41
15.38	18.5	2.70	1.02	0.30	7.5	6.6	1.7	1.5	5.6	4.9	9.53	9.45
18.48	17.5	2.65	1.01	0.264	7.2	6.2	1.6	1.3	4.6	4.1	9.56	9.48
23.39	16	2.58	1.00	0.219	6.8	5.6	1.4	1.1	3.3	3.0	9.59	9.53
29.84	18	2.47	0.97	0.170	7.3	6.2	2.3	1.3	2.8	2.5	9.57	9.49
36.38	18	2.37	0.94	0.129	6.6	6.0	1.4	1.2	2.3	1.9	9.56	9.50
43.20	18.5	2.27	0.92	0.096	6.6	6.0	1.6	1.3	1.6	1.4	9.65	9.50
50.55	17.5	2.17	0.90	0.069	5.7	5.3	1.1	1.]	1.3	1.0	9.71	9.51
58.47	18.5	2.07	0.88	0.048	5.5	5.2	1.6	1.5	0.83	0.78	9.73	9.47
66.78	20	1.96	0.85	0.033	5.4	5.4	1.5	1.7	0.61	0.61	9.72	9.43
75.44	20	1.86	0.81	0.022	5.1	5.2	1.8	1.8	0.46	0.38	9.68	9.43

TABLE B-1 (Continued)

SRC Process Condensate Stripping (500mL)

ft ³ N ₂ ^a	T ^o C	Concentration Moles/Liter			Vapor pressure				mmHg		pH	
		NH ₃	CO ₂	H ₂ S	P _{NH₃}		P _{CO₂}		P _{H₂S}		exp.	calc. ^b
					exp.	calc. ^b	exp.	calc. ^b	exp.	calc. ^b		
84.86	19	1.76	0.78	0.013	4.4	4.6	1.5	1.6	0.26	0.22	9.56	9.45
95.84	19	1.64	0.70	0.0029	3.8	4.7	1.4	1.3	0.045	0.044	9.45	9.49
108.65	18	1.51	0.64	0.0017	3.2	4.4	1.2	1.3	0.032	0.026	9.46	9.50
122.99	19	1.38	0.58	0.0007	3.0	4.1	1.3	1.2	0.024	0.010	9.45	9.50
140.17	16	1.25	0.50	0.0001	2.2	3.4	1.0	0.72	0.0045	0.0011	9.49	9.63
160.61	17	1.13	0.42	-	2.0	3.7	1.0	0.58	-	-	9.57	9.67
181.40	20	1.00	0.34	-	2.2	4.4	1.1	0.55	-	-	9.55	9.66
203.47	19.5	0.87	0.26	-	1.8	4.3	0.87	0.34	-	-	9.47	9.76
229.74 ^c	20	0.76	0.181	-	1.6	4.5	0.79	0.18	-	-	9.45	9.89
262.09 ^c	20	0.67	0.097	-	1.21	5.0	0.51	0.049	-	-	9.39	10.15
299.05 ^c	19	0.60	0.0417	-	0.68	5.0	0.18	0.0082	-	-	9.26	10.50
338.67 ^c	18	0.56	0.0194	-	0.41	4.76	0.072	0.0016	-	-	9.07	10.79
402.26 ^c	19	0.54	0.0092	-	0.18	4.98	0.015	0.0004	-	-	8.65	11.02

a. ft³ as saturated N₂b. Calculations based on only NH₃- CO₂- H₂S - H₂O presentc. Corrected to ft³/500mL

TABLE B-2
SRC Process Condensate Stripping (500mL)

ft ³ N ₂ ^a	T ^o C	Concentration Moles/Liter			Vapor pressure				mm Hg		pH	
		NH ₃	CO ₂	H ₂ S	P _{NH₃}		P _{CO₂}		P _{H₂S}		exp.	calc. ^b
					exp.	calc. ^b	exp.	calc. ^b	exp.	calc. ^b		
0.35	19	2.95	1.23	0.87	4.6	1.2	25.2	29.1	43.6	125	8.84	8.53
1.26	20	2.94	1.18	0.80	4.9	1.7	20.8	20.0	27.0	85	8.97	8.65
2.67	20	2.92	1.14	0.72	5.6	2.2	9.8	13.7	21.3	58.4	9.13	8.76
4.54	20	2.89	1.11	0.63	7.0	2.6	5.8	10.2	17.8	41.2	9.28	8.85
6.82	20	2.86	1.08	0.56	7.7	3.1	4.2	7.8	12.4	30.2	9.39	8.93
9.54	20	2.81	1.06	0.49	7.9	3.3	3.2	6.7	9.1	23.8	9.47	8.98
2.43	19	2.76	1.04	0.35	8.0	3.8	2.5	4.3	6.7	12.4	9.50	9.11
15.38	18.5	2.70	1.02	0.30	7.5	3.7	1.7	3.9	5.6	9.9	9.53	9.15
18.48	17.5	2.65	1.01	0.264	7.2	3.4	1.6	3.5	4.6	8.3	9.56	9.17
23.39	16	2.58	1.00	0.219	6.8	3.0	1.4	3.1	3.3	6.4	9.59	9.21
29.84	18	2.47	0.97	0.170	7.3	3.4	2.3	3.7	2.8	5.3	9.57	9.17
36.38	18	2.37	0.94	0.129	6.6	3.2	1.4	3.7	2.3	4.1	9.56	9.17
43.20	18.5	2.27	0.92	0.096	6.6	3.1	1.6	4.0	1.6	3.1	9.65	9.15
50.55	17.5	2.17	0.90	0.069	5.7	2.7	1.1	4.1	1.3	2.3	9.71	9.15
58.47	18.5	2.07	0.88	0.048	5.5	2.5	1.6	5.1	0.83	1.8	9.73	9.08
66.78	20	1.96	0.85	0.033	5.4	2.6	1.5	6.2	0.61	1.4	9.72	9.02
75.44	20	1.86	0.81	0.022	5.1	2.3	1.8	6.6	0.46	1.0	9.68	9.00

TABLE B-2 (Continued)

SRC Process Condensate Stripping (500mL)

ft ³ N ₂ ^a	T ^o C	Concentration Moles/Liter			Vapor pressure mm Hg						pH	
		NH ₃	CO ₂	H ₂ S	P _{NH₃}		P _{CO₂}		P _{H₂S}		exp.	calc. ^b
					exp.	calc. ^b	exp.	calc. ^b	exp.	calc. ^b		
84.86	19	1.76	0.78	0.013	4.4	1.4	1.5	6.7	0.26	0.62	9.56	8.99
95.84	19	1.64	0.70	0.0029	3.8	1.9	1.4	6.1	0.045	0.13	9.45	9.01
108.65	18	1.51	0.64	0.0017	3.2	1.7	1.2	6.6	0.032	0.087	9.46	8.97
122.99	19	1.38	0.58	0.0007	3.0	1.4	1.3	7.3	0.024	0.038	9.45	8.92
140.17	16	1.25	0.50	0.0001	2.2	1.0	1.0	5.5	0.0045	0.0050	9.49	8.97
160.61	17	1.13	0.42	-	2.0	1.0	1.0	5.3	-	-	9.57	8.95
181.40	20	1.00	0.34	-	2.2	1.1	1.1	5.7	-	-	9.55	8.87
203.47	19.5	0.87	0.26	-	1.8	0.91	0.87	5.3	-	-	9.47	8.83
229.74 ^c	20	0.76	0.181	-	1.6	0.83	0.79	4.1	-	-	9.45	8.81
262.09 ^c	20	0.67	0.097	-	1.21	0.96	0.51	1.7	-	-	9.39	8.92
219.05 ^c	19	0.60	0.0417	-	0.68	0.92	0.18	0.61	-	-	9.26	9.00
238.67 ^c	18	0.56	0.0194	-	0.41	0.78	0.072	0.29	-	-	9.07	8.99
402.26 ^c	19	0.54	0.0092	-	0.18	0.76	0.015	0.17	-	-	8.65	8.94

a. ft³ as saturated N₂.

b. Calculations based on 0.45N non-volatile anions and additional ionic strength of 0.36M present in condensate.

c. Corrected to ft³/500mL.

TABLE B-3
SRC Prestripped Process Condensate Stripping (500mL)

ft ³ N ₂ ^a	T°C	Concentration Moles/Liter		Vapor pressure mmHg				pH	
				P _{NH₃}		P _{CO₂}			
		NH ₃	CO ₂	exp.	calc. ^b	exp.	calc. ^b	exp.	calc. ^b
240 ^c	20	0.70	0.100	1.08	5.3	0.38	0.047	9.51	10.16
280	22	0.61	0.047	0.76	5.8	0.25	0.014	9.31	10.37
320	21	0.546	0.017	0.385	5.4	0.058	0.0017	9.03	10.74
375	20.5	0.511	0.0093	0.200	5.1	0.011	0.0005	8.79	10.95
416	21.5	0.491	0.0078	0.103	5.1	0.0082	0.0004	8.52	10.97
470	22	0.478	0.006	0.051	5.1	0.0042	0.0003	8.25	11.03
525	23	0.473	0.004	0.034	5.4	-	0.0001	7.99	11.12
685	21	0.468	0.002	0.020	4.9	-	-	7.69	11.38

a. ft³ as saturated N₂.

b. Calculations assuming only NH₃ - CO₂ - H₂S - H₂O present.

c. Approximately 220 ft³/500mL were passed through before measurement began.

TABLE B-4

SRC Prestripped Process Condensate Stripping (500mL)

ft ³ N ₂ ^a	T ^o C	Concentration Moles/Liter		Vapor pressure		mmHg		pH	
				P _{NH₃}		P _{CO₂}			
		NH ₃	CO ₂	exp.	calc. ^b	exp.	calc. ^b	exp.	calc. ^b
240 ^c	20	0.70	0.100	1.08	1.18	0.38	1.31	9.51	9.01
280	22	0.61	0.047	0.76	1.10	0.25	0.88	9.31	8.91
320	21	0.546	0.017	0.385	0.81	0.058	0.39	9.03	8.86
375	20.5	0.511	0.0093	0.200	0.54	0.011	0.31	8.79	8.72
416	21.5	0.491	0.0078	0.103	0.39	0.0032	0.46	8.52	8.52
470	22	0.478	0.006	0.051	0.28	0.0042	0.54	8.25	8.36
525	23	0.473	0.004	0.034	0.26	-	0.44	7.99	8.28
685	21	0.468	0.002	0.020	0.21	-	0.21	7.69	8.29

a. ft³ as saturated N₂.

b. Calculations based on 0.45N non-volatile anions and additional ionic strength of 0.36M present in condensate.

c. Approximately 220 ft³/500mL were passed through before measurement began.

TABLE B-5

Measured Concentrations vs.
Absorber Mass Balances

ft ³ N ₂ ^a	Concentration		Moles/Liter			
	NH ₃		CO ₂		H ₂ S	
	b	c	b	c	b	c
0	2.95 ^d	2.95	1.25 ^d	1.25	0.91 ^d	0.91
0.70	2.94	2.94	1.20	1.21	0.83	0.84
1.82	2.93	2.93	1.16	1.16	0.75	0.77
3.51	2.90	2.91	1.12	1.12	0.68	0.70
5.56	2.87	2.88	1.09	1.09	0.59	0.61
8.08	2.83	2.83	1.07	1.07	0.52	0.54
10.99	2.78 ^d	2.78	1.05 ^d	1.05	0.42 ^d	0.48
13.86	2.73	2.73	1.03	1.03	0.33	0.44
16.90	2.68	2.68	1.01	1.02	0.28	0.40
20.06	2.61	2.62	1.00	1.01	0.24	0.37
26.71	2.52	2.53	0.98	0.99	0.19	0.32
32.97	2.42	2.43	0.96	0.97	0.15	0.28
39.77	2.32	2.33	0.93	0.94	0.11	0.24
46.62	2.22	2.23	0.91	0.92	0.08	0.22
54.48	2.12	2.13	0.89	0.90	0.05	0.19
62.46	2.01	2.02	0.86	0.87	0.04	0.18
71.10	1.91	1.92	0.83	0.84	0.03	0.17
79.78	1.81	1.82	0.79	0.80	0.02	0.16
89.94	1.70 ^d	1.72	0.74 ^d	0.76	0.01 ^d	0.15
101.74	1.58	1.61	0.67	0.73	-	0.15
115.56	1.44	1.51	0.61	0.69	-	0.15
130.41	1.31	1.41	0.54	0.65	-	0.15
149.93	1.19	1.31	0.46	0.60	-	0.15
171.38	1.06	1.21	0.38	0.55	-	0.15
191.41	0.93	1.11	0.30	0.50	-	0.15
215.52	0.80 ^d	1.01	0.22 ^d	0.45	- ^d	0.15

TABLE B-5 (Continued)

Measured Concentrations vs.
Absorber Mass Balances

	Concentration		Moles/Liter			
	NH ₃		CO ₂		H ₂ S	
ft ³ N ₂ ^a	b	c	b	c	b	c
243.96 ^e	0.71	0.91	0.14	0.40	-	0.15
280.22 ^e	0.63	0.81	0.07	0.36	-	0.15
317.88 ^e	0.58	0.75	0.03	0.34	-	0.15
359.46 ^e	0.55	0.71	0.01	0.34	-	0.15
445.06 ^e	0.53 ^d	0.69	- ^d	0.33	- ^d	0.15

a. ft³ as saturated N₂.

b. Interpolated from measured concentrations.

c. From absorber mass balances alone.

d. Actual measured concentration.

Appendix C

Omega-9 Retort Water Stripping Data

The stripping data of Omega-9 retort water is shown in Tables C-1 and C-2. Table C-1 is a comparison of experimental data and calculated values based on 0.07 N excess cations and 0.204 M additional ionic strength. Table C-2 is a comparison based on 0.105 N excess cations and 0.204 M additional ionic strength. The cubic feet passed through are based on 250 ml solution ($\text{ft}^3/250 \text{ ml}$). The amounts of cubic feet passed through, concentrations, vapor pressures, and pH values are the average of the values at the beginning and end of bubbling intervals.

TABLE C-1

Omega-9 Retort Water Stripping (250mL)

ft ³ N ₂ ^a	T°C	Concentration Moles/Liter		Vapor pressure mmHg				pH	
				P _{NH₃}		P _{CO₂}		exp.	calc. ^b
		NH ₃	CO ₂	exp.	calc. ^b	exp.	calc. ^b		
0.30	21.5	0.217	0.272	0.35	0.067	6.90	52.8	8.77	8.11
0.91	21.0	0.216	0.253	0.46	0.13	5.95	21.9	9.01	8.44
1.66	21.5	0.314	0.236	0.54	0.20	4.06	12.9	9.12	8.63
2.67	23.0	0.212	0.220	0.68	0.30	3.13	9.0	9.20	8.75
4.19	18.0	0.208	0.203	0.56	0.27	1.90	4.2	9.34	8.99
6.38	20.0	0.201	0.186	0.70	0.38	1.38	3.2	9.43	9.07
9.15	20.0	0.191	0.171	0.73	0.41	1.08	2.4	9.49	9.14
12.75	20.0	0.179	0.155	0.79	0.45	0.80	1.7	9.57	9.22
16.71	20.0	0.166	0.142	0.71	0.46	0.61	1.37	9.63	9.28
20.71	20.0	0.153	0.133	0.72	0.44	0.51	1.22	9.66	9.30
24.54	20.5	0.141	0.125	0.69	0.44	0.41	1.13	9.67	9.32
27.96	19.5	0.130	0.119	0.64	0.39	0.34	0.96	9.68	9.36
31.37	20.5	0.120	0.114	0.61	0.34	0.36	0.99	9.69	9.34
35.14	19.0	0.111	0.108	0.54	0.34	0.28	0.82	9.71	9.39
39.35	20.0	0.101	0.103	0.54	0.33	0.26	0.84	9.74	9.37
43.31	21.0	0.091	0.099	0.51	0.31	0.24	0.40	9.75	9.34
47.14	21.0	0.083	0.095	0.46	0.29	0.22	0.87	9.75	9.34
51.02	21.0	0.075	0.091	0.43	0.26	0.19	0.83	9.77	9.34

TABLE C-1 Continued
Omega-9 Retort Water Stripping (250mL)

ft ³ N ₂ ^a	T°C	Concentration Moles/Liter		Vapor pressure mmHg				pH	
				P _{NH₃}		P _{CO₂}		exp.	calc. ^b
		NH ₃	CO ₂	exp.	calc. ^b	exp.	calc. ^b		
55.19	20.0	0.067	0.088	0.37	0.22	0.161	0.79	9.79	9.35
59.36	20.5	0.060	0.085	0.335	0.20	0.143	0.82	9.80	9.34
63.37	20.5	0.054	0.083	0.314	0.18	0.129	0.85	9.83	9.32
67.90	20.0	0.0478	0.0804	0.266	0.15	0.118	0.89	9.86	9.31
72.64	19.5	0.0418	0.0779	0.239	0.12	0.110	0.82	9.91	9.31
77.55	19.5	0.0365	0.0756	0.212	0.11	0.094	0.82	9.93	9.30
82.53	19.5	0.0316	0.0737	0.187	0.090	0.083	0.85	9.89	9.28
81.14	20.0	0.0267	0.0722	0.168	0.080	0.077	0.91	9.87	9.26
92.04	20.5	0.0238	0.0707	0.155	0.070	0.070	0.97	9.88	9.23
91.65	21.0	0.0199	0.0691	0.135	0.059	0.068	1.03	9.91	9.21
104.75	19.5	0.0159	0.0672	0.099	0.042	0.053	0.95	9.94	9.22
114.10	20.0	0.0118	0.0654	0.078	0.031	0.042	1.02	9.99	9.19
123.41	21.0	0.0085	0.0639	0.061	0.024	0.041	1.10	10.01	9.16
132.53	22.0	0.0061	0.0626	0.045	0.018	0.031	1.15	10.04	9.14
142.63	21.5	0.0041	0.0616	0.033	0.012	0.024	1.13	10.10	9.14
152.91	21.5	0.0022	0.0609	0.019	0.0075	0.018	1.15	10.15	9.13

a. ft³ as saturated N₂.

b. Calculations based on 0.07 N excess nonvolatile cations and additional ionic strength of 0.204M present in retort water.

TABLE C-2
Omega-9 Retort Water Stripping (250mL)

ft ³ N ₂ ^a	T°C	Concentration Moles/Liter		Vapor pressure mmHg				pH	
				P _{NH₃}		P _{CO₂}		exp.	calc. ^b
		NH ₃	CO ₂	exp.	calc. ^b	exp.	calc. ^b		
0.30	21.5	0.217	0.272	0.35	0.18	6.90	16.3	8.77	8.59
0.91	21.0	0.216	0.253	0.46	0.26	5.95	9.21	9.01	8.78
1.66	21.5	0.214	0.236	0.54	0.34	4.06	6.19	9.12	8.91
2.67	23.0	0.212	0.220	0.68	0.47	3.13	4.63	9.20	8.99
4.19	18.0	0.208	0.203	0.56	0.40	1.90	2.22	9.34	9.21
6.38	20.0	0.201	0.186	0.70	0.53	1.38	1.71	9.43	9.28
9.15	20.0	0.191	0.171	0.73	0.57	1.08	1.27	9.49	9.35
12.75	20.0	0.179	0.155	0.79	0.61	0.80	0.89	9.57	9.44
16.71	20.0	0.166	0.142	0.71	0.63	0.61	0.68	9.63	9.51
20.71	20.0	0.153	0.133	0.72	0.62	0.51	0.57	9.66	9.54
24.54	20.5	0.141	0.125	0.69	0.61	0.41	0.51	9.67	9.57
27.96	19.5	0.130	0.119	0.64	0.56	0.34	0.41	9.68	9.62
31.37	20.5	0.120	0.114	0.61	0.56	0.36	0.40	9.69	9.62
35.14	19.0	0.111	0.108	0.54	0.49	0.28	0.31	9.71	9.69
39.35	20.0	0.101	0.103	0.54	0.49	0.26	0.30	9.74	9.69
43.31	21.0	0.091	0.099	0.51	0.48	0.24	0.30	9.75	9.68
47.14	21.0	0.083	0.095	0.46	0.45	0.22	0.27	9.75	9.70
51.02	21.0	0.075	0.091	0.43	0.42	0.19	0.24	9.77	9.73

TABLE C-2 Continued
Omega-9 Retort Water Stripping (250mL)

ft ³ N ₂ ^a	T°C	Concentration Moles/Liter		Vapor pressure mmHg				pH	
				P _{NH₃}		P _{CO₂}		exp.	calc. ^b
		NH ₃	CO ₂	exp.	calc. ^b	exp.	calc. ^b		
55.19	20.0	0.067	0.088	0.37	0.36	0.161	0.21	9.79	9.76
59.36	20.5	0.060	0.085	0.335	0.338	0.143	0.20	9.80	9.77
63.37	20.5	0.054	0.083	0.314	0.308	0.129	0.190	9.83	9.78
67.90	20.0	0.0478	0.0804	0.266	0.268	0.118	0.169	9.86	9.81
72.64	19.5	0.0418	0.0779	0.239	0.232	0.110	0.149	9.91	9.84
77.55	19.5	0.0365	0.0756	0.212	0.208	0.094	0.133	9.93	9.87
82.53	19.5	0.0316	0.0737	0.187	0.183	0.083	0.122	9.89	9.88
87.14	20.0	0.0276	0.0722	0.168	0.167	0.077	0.117	9.87	9.89
92.04	20.5	0.0238	0.0707	0.155	0.151	0.070	0.111	9.88	9.90
97.65	21.0	0.0199	0.0691	0.135	0.133	0.068	0.103	9.91	9.92
104.75	19.5	0.0159	0.0672	0.099	0.100	0.053	0.080	9.94	9.98
114.70	20.0	0.0118	0.0654	0.078	0.079	0.042	0.070	9.99	10.01
123.41	21.0	0.0085	0.0639	0.061	0.062	0.041	0.063	10.01	10.03
132.53	22.0	0.0061	0.0626	0.045	0.049	0.031	0.055	10.04	10.06
142.63	21.5	0.0041	0.0616	0.033	0.033	0.024	0.047	10.10	10.10
152.91	21.5	0.0022	0.0609	0.019	0.021	0.018	0.042	10.15	10.18

a. ft³ as saturated N₂.

b. Calculations based on 0.105 N excess nonvolatile cations and additional ionic strength of 0.204M present in retort water.

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